THE CHEMISTRY OF LEATHER MANUFACTURE

BY

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GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, Secretary of the American Chemical Society, Washington, D. C.; John E. Teeple, Treasurer of the American Chemical Society, New York City; and Professor Gellert Alleman of Swarthmore College. The Trustees have arranged for the publication of the American Chemical Society series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company of New York City.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed the editors, named at the close of this introduction, to have charge of securing authors, and of considering critically the manuscripts prepared. The editors of each series will endeavor to select topics which are of current interest and authors who are recognized as authorities in their respective fields. The list of monographs thus far secured appears in the publisher's own announcement elsewhere in this volume.

The development of knowledge in all branches of science, and especially in chemistry, has been so rapid during the last fifty years and

the fields covered by this development have been so varied that it is difficult for any individual to keep in touch with the progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and such compendia as Beilstein's Handbuch der Organischen Chemie, Richter's Lexikon, Ostwald's Lehrbuch der Allgemeinen Chemie, Abegg's and Gmelin-Kraut's Handbuch der Anorganischen Chemie and the English and French Dictionaries of Chemistry, it often takes a great deal of time to coördinate the knowledge available upon a single topic. Consequently when men who have spent years in the study of important subjects are willing to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value to their fellow chemists.

It was with a clear recognition of the usefulness of reviews of this character that a Committee of the American Chemical Society recommended the publication of the two series of monographs under the auspices of the Society.

Two rather distinct purposes are to be served by these monographs. The first purpose, whose fulfillment will probably render to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a readable form, intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs will enable such men to form closer contact with the work of chemists in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well digested survey of the progress already made in that field and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, it is intended to include extended references to the literature, which will enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection will be made of those papers which are most important.

The publication of these books marks a distinct departure in the policy of the American Chemical Society inasmuch as it is a serious attempt to found an American chemical literature without primary regard to commercial considerations. The success of the venture will depend in large part upon the measure of coöperation which can be secured in the preparation of books dealing adequately with topics of

general interest; it is earnestly hoped, therefore, that every member of the various organizations in the chemical and allied industries will recognize the importance of the enterprise and take sufficient interest to justify it.

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PREFACE

The chemistry of leather manufacture is progressing more rapidly now than at any previous time. Much of the earlier work failed to recognize the existence of important variable factors and has been rendered obsolete by recent investigations carried out under more highly refined conditions. In preparing this monograph, it was found necessary, for the purpose of correlating existing data, to conduct many special investigations and these are being reported here for the first time. Advance information on investigations under way in other laboratories has been obtained, wherever possible, so that the presentation might be made reasonably complete to the close of the year 1922.

The literature pertaining to leather manufacture is so vast and the views expressed so numerous and divergent as to make an impersonal compilation of all published papers encyclopedic in size, bewildering to the average reader, and an undertaking of questionable value. In order to fulfill the first purpose of this series of monographs, namely, to present the knowledge available in a readable form, intelligible to those whose activities may be along a wholly different line, the author has felt compelled to present the subject from his own viewpoint, making no attempt to discuss views which, in his opinion, fail to contribute anything to the development of leather chemistry. In so doing, the author is fully aware that there are others who do not share his opinions of the relative merits of various views, but he can only admit his inability to present adequately views which appear to him unsound. But, in a field so vast, there is ample room for as many volumes as there may be sides to the question worthy of presentation and it is in the preparation of additional volumes that criticism of this attitude may find its best expression.

A considerable amount of space has been devoted to the histology of skin and to the physical chemistry of the proteins because of their fundamental bearing on the chemistry of leather manufacture. Descriptions of analytic methods and practical details of leather manufacture have been given only where they seemed necessary to make the subject clearer to chemists unfamiliar with tannery routine.

Many of the ideas presented in this book were gained during a

period of intimate association with Professor H. R. Procter, of the University of Leeds, England, who is affectionately known throughout the world as the "father of leather chemistry" and whose books on leather manufacture have been the standard for the past thirty-five years.

In the preparation of sections and photomicrographs, valuable assistance was rendered by Mr. Guido Daub, whose painstaking efforts are largely responsible for the success of this phase of the work. The sections and specimens of human skin were procured from Professor T. H. Bast, of the University of Wisconsin. Professor Arthur W Thomas, of Columbia University, supplied the skins of guinea pigs and albino rats fixed in Erlicki's fluid. Leathers from the hides of the hippopotamus, walrus, and camel were furnished by Professor Douglas McCandlish, of the University of Leeds. Most of the remaining specimens were provided by the firm of A. F. Gallun & Sons Company, in whose laboratories the work was done. The interesting photographs illustrating the drying of gelatin blocks were furnished by Dr. S. E. Sheppard, of the Eastman Kodak Company.

Grateful acknowledgment is made of the generous criticisms and suggestions given by Mrs. Marion Hines Loeb, of the University of Chicago, on the general histology of skin; by Dr. Jacques Loeb, of the Rockefeller Institute, on the physical chemistry of the proteins; and by Professor A. W. Thomas, Mr. Frank L. Seymour-Jones, and Miss Margaret W. Kelly, of Columbia University, on many important points throughout the book.

The author is most deeply indebted to the late Arthur H. Gallun, whose devotion to the cause of leather chemistry has made available a large portion of the data presented in this book.

J. A. W.

Milwaukee, Wisconsin,
March 12, 1923.

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THE CHEMISTRY OF LEATHER MANUFACTURE

Chapter I.

Introduction.

Leather chemistry is one of the most fascinating branches of industrial chemistry and also one of the most complex, dealing, as it does, with reactions between those poorly defined groups of substances, usually colloidal, whose compositions are still matters for speculation. The raw skin is composed largely of various kinds of protein matter and is complicated by a structure which varies considerably in different animals and even in different parts of the same skin. Conversion into leather involves the removal of some of these proteins by the action of alkalies, enzymes, or bacteria, and the interaction of the remainder with tanning materials, oils, soaps, emulsions, mordants, dyestuffs, gums, resins, and other complex materials. During these reactions the structure of the skin must be carefully preserved, or improved, and highly developed technic is required to impart to the resulting leather certain necessary, but almost indefinable, properties, many of which it is an art even to appreciate fully. When one considers the vast amount of energy expended by organic chemists upon the materials involved in making leather and the uncertainty of our knowledge concerning the individual substances, the complexity of the whole problem becomes more apparent.

Leather manufacture as an art probably antedates chemistry as a science. Well preserved specimens of leather from ancient Egypt bear testimony to the high state of development of the art over three thousand years ago. Its origin presumably dates back to the time when man first began to kill animals for food. The skins, not being palatable, were very likely discarded at first, but the value of dried skins for clothing, or protective covering, could hardly remain long undiscovered. Dried skins are hard and stiff, but would become considerably softer and more pliable after being bent and worked during use, and it was probably noticed very early that this softening action is more pronounced if the skins are worked while being dried, especially in the presence of fats, such as would naturally cling to the skins of animals crudely flayed. In rainy seasons, when the skins could not

be dried rapidly, putrefaction of the epidermal cells would cause the hair to slip and reveal the advantages of unhaired skins for certain purposes. The tanning and coloring actions of leaves, barks, and woods were probably also accidental discoveries of a prehistoric age. In fact, many of the tannery operations in use today are of ancient origin.

Secrecy and lack of accurate records make it difficult to follow the evolution of the art, especially in the matter of details essential to the production of the finer qualities of leather. But developments have not all been made by rule-of-thumb methods, as has often been supposed. The great success of a certain class of tanners, for example, has been due to the development of a science of leather manufacture, as distinct from the art, based upon a belief in the constancy of natural laws and involving the organization and classification of countless facts gained by experience or handed down from previous generations. This science, because of its high degree of specialization, has proved more powerful in a practical way than chemistry, so much so that chemistry must still be regarded as of value primarily in supplementing and not replacing the science of the tanner.

Disillusionment has been common among chemists entering this industry, as the result of the unexpected intricacy of the application of chemistry to leather manufacture, of insufficient training, of false notions of superiority over artisans who had devoted their lives to the industry, or of failure to appreciate that the tanner's own science is usually far more reliable than the chemistry of a beginner in the industry.

In order to make substantial progress, the chemist must, as a rule, devote himself completely to a study and explanation of the mechanism of each step of a process already in successful operation and without in any way interfering with the operation of that process. Once available, sound explanations of the mechanism of existing processes are of incalculable value in suggesting practical experiments leading to the elimination of unnecessary operations and to the improvement and development of others.

That this procedure has not been more widely adopted is easily explained. Long and costly studies are required for which there is no immediate return, and whether there will ever be a return commensurate with the cost of the studies must depend upon the skill of the chemist, which it is difficult for the tanner to judge. Moreover, the qualifications required of the chemist are extremely severe. He must have a broad, theoretical training, marked ability to advance the pure science, great skill in adapting delicate apparatus to crude, tannery conditions, and power to appreciate the viewpoint of a successful tanner. Previous contact with the industry, on the other hand, is not essential.

That close coöperation between the university and the industry would be highly profitable to both cannot be denied, but there is little chance of such coöperation being brought about until each acquires a better understanding of the needs and potentialities of the other. The stumbling block has been either the failure to appreciate the value

of coöperation or the disinclination of one or the other to take the initiative.

The university can derive at least three important lines of advantage from coöperation with the industry, the most obvious of which is much needed financial support. But the laws of the conservation of mass and energy hold in industry, as in everything else. The university cannot continue to receive from the industry without returning a like amount, although this may be of a different kind. The university has vast resources of potential wealth, but it suffers from having too little in liquid form. But industry constitutes a means of converting one form of wealth into another. The university can be assured a continuous financial support from the industry, but only by supplying the industry with the means of producing this wealth.

Another advantage to be gained by the university is the viewpoint of the industry, which is necessary for the university to prepare its potential wealth so that it may be assimilated by the industry. This viewpoint will also help the university to train its students to make a greater success in industry. The third advantage lies in the fact that the industry offers a field of employment for the students of the university. The industry is always in need of men properly trained from its own viewpoint. But, too often, the training which men receive at the university does not equip them with a power of service to the industry that is in demand at all times. Through closer coöperation a system of training could be devised that would guarantee the opportunities of industry to men with initiative and ambition.

The source of wealth that coöperation offers to the industry consists of fundamental data and of men trained to apply these data to practical production. The possibilities for increasing efficiency in the industry are almost unlimited and so are the profits to be derived by both the university and the industry from intelligent coöperation.

Chemists within the industry have always been handicapped by lack of fundamental information. Many of the physical properties that determine the value of leather are determined by its microscopic structure, but very few tanneries have found themselves in a position to develop the means for studying the histology and chemical constituents of skin and the structure of leathers made under different conditions. Such studies are expensive and time consuming and their development in each individual tannery would be very extravagant. The industry could well afford to finance a laboratory to be devoted solely to such studies, which would probably cover a period of many years. That a good start has been made will be evident from a perusal of the next chapter.

The physical chemistry of the proteins is a subject of fundamental importance to leather chemistry, but, since it is also of fundamental importance to many other branches of chemistry, it should be possible for some good university laboratory to establish a great scheme for co-operative work in this field, drawing financial support from

many different fields. A university research laboratory is also an ideal place in which to study both the physical and organic chemistry of the proteins and the natural tannins. Physical chemistry offers much the better prospects for immediate application to manufacturing practice, but both should be developed simultaneously.

There is hardly any fundamental work in leather chemistry that is not suitable for the university laboratory, but, in order to command the financial support of the industry, it must be done in such a way as to make it directly serviceable to the industry. Appreciating the inertia that must be overcome before any great research movement can gain sufficient momentum to make it practically self-supporting, the late Arthur H. Gallun, with remarkable foresight and loftiness of purpose, established a research in the fundamentals of leather chemistry, under the direction of Professor A. W. Thomas, of Columbia University, with the proviso that all results be published freely for the benefit of the industry as a whole. The results obtained during the past few years compare favorably with all previous work done on the mechanism of chrome and vegetable tanning. It will be evident from the description of this work, in the later chapters, that it must ultimately prove of great practical value and it is difficult to see how it can fail to gain the support of the entire industry in due time. It is worthy of special mention here as a demonstration of a kind of coöperation that should prove very profitable to both the university and the industry.

It is hoped that the following pages will give chemists in many fields a better understanding of the problems of the leather industry and of the opportunities for coöperative research, and also give the industry itself a clearer appreciation of the possibilities for further extending the application of pure chemistry to leather manufacture.

Chapter 2.

Histology of Skin.

Since animal skin is the basis of leather, the importance of its histology to the science of leather manufacture is apparent. Nevertheless scientific advancement, especially in regard to the preparation of skin for tanning, has been retarded by an insufficient knowledge of the histology of the skins of animals used in making leather. This has been due less, perhaps, to lack of appreciation of the value of histology than to the high degree of refinement of equipment and technic required for its study.

Much of the complexity of the structure of the skin is due to the manifold purposes it serves. As a means of protection for the underlying organs, it is so constructed as to act as a buffer against shocks or blows, while not interfering with the operation of any organs. It is an organ of sense, equipped with nerves sensitive to touch, pain, heat and cold, and, as an organ of secretion and excretion, it is supplied with glands, ducts, muscles, and blood vessels. It serves also as a regulator of the body temperature, which it controls by regulating the evaporation of water from its surface and the secretion of oil to cover the surface in order to prevent too great a loss of heat.

The degree to which each constituent part of the skin is developed depends upon the extent to which it is needed by the body and also upon the amount of available nourishment. The structure of a single skin varies considerably in different regions of the body. Nerve papillæ, for example, are very numerous in regions where the sense of touch is most needed, as in the finger tips, and widely scattered in other regions. The skin structure is developed to meet sudden changes of temperature to the greatest extent in the regions of the body most exposed to such changes and to resist friction and blows where these are most frequent. In fact, the skin tends to develop a structure at each point designed to be of greatest service to the body at that point. This results in a large number of types of skin structure that must be studied, depending upon the species of animal, the general nature of its feeding, the climatic conditions under which it lived, and the region of the body from which the specimen is taken.

The number of possible types appears formidable, but tanners have learned from experience how to classify them in a general way according to the properties of the leather they yield. It seems reasonable to believe that histologists may be able to develop a similar classification, based upon histology, that will prove extremely valuable in supplementing the tanners' information.

Because of the large number of highly trained investigators in the medical sciences, considerable progress has been made in the histology of human skin. This work is invaluable as a guide to the student of the histology of the skins of lower animals because most skins possess a common basic structure. But the several types of skin exhibit such marked differences in details of structure of vital importance in leather manufacture that a knowledge of the histology of a few specimens of human skin alone might actually be misleading. In order to apply histology intelligently to leather manufacture, separate studies must be made of the structure of each type encountered.

Although much yet remains to be learned of the histology of skins used for leather manufacture, substantial progress has been made, the most notable work being that of Alfred Seymour-Jones.[1] Systematic studies have also been under way in the author's laboratories, for several years, dealing with the structure of the skins of different animals and the changes which they undergo during the conversion of the skin into leather. In this book much of this work is presented for the first time.

Preparation of Sections and Photomicrographs for Study.

Since much of the information given in this chapter was obtained by direct observation of sections prepared in the author's laboratories, a description of the methods employed will probably assist in making the presentation clearer, particularly so in view of the fact that work of this kind appears not to have been general in tannery laboratories. The description, however, will be limited to the methods used in the production only of the photomicrographs appearing in this book. The subjects of microscopy, microtomy, and photomicrography are too vast in scope for adequate treatment here and the reader desiring to pursue these subjects further is referred to the several excellent works available, such as those of Gage[2] and Lee.[3]

Sampling.—In studying the entire skin of an animal, strips of about 0.5 x 2 inches were cut from different parts of the skin so as to show, not only the general structure, but also its variation throughout the skin. Care was taken, in cutting the strips, so that the later sectioning could be done in definite planes, as, for example, that including a hair follicle and erector pili muscle. It was found important that the plane selected be uniform for any given series of sections showing changes taking place during the passage of a skin through the tannery processes.

Fixing.—After a tissue dies, the structure undergoes a gradual change unless it is immediately *fixed*. According to Lee, the word *fixing* implies two things: "first, the rapid *killing* of the element, so that it may not have time to change the form it had during life, but is fixed in death in the attitude it normally had during life; and

[1] Physiology of the Skin. Alfred Seymour-Jones. *J. Soc. Leather Trades' Chem.*, serially 1917-21.

[2] The Microscope. S. H. Gage. Comstock Publishing Co., Ithaca, N. Y.

[3] The Microtomist's Vade-Mecum. A. B. Lee. P. Blakiston's Son & Co., Philadelphia, Pa.

second, the *hardening* of it to such a degree as may enable it to resist without further change of form the action of the reagents with which it may subsequently be treated. *Without good fixation it is impossible to get good stains or good sections, or preparations good in any way.*"

The photomicrographs shown in this book are from sections fixed either in Erlicki's fluid or in alcohol. Numerous other fixing agents were tried, but they did not answer so well for the specific purposes in view. Erlicki's fluid is made simply by dissolving 25 grams of potassium dichromate and 10 grams of copper sulfate in a liter of water. The strips of fresh skin were placed directly into this solution without previous washing. They were transferred to fresh solutions daily for the first 3 days and then kept in the last bath until the solution had thoroughly penetrated them. The period of contact was usually from 5 to 7 days, after which they were washed in running tap water for about 20 hours and then dehydrated with alcohol.

The skins of the sheep, cow, calf, and guinea pig, whose sections are shown in this book, were fixed immediately after the animals were killed. Their sections may, therefore, be regarded as showing the normal structure of the living skin. The other sections exhibit structures of skins as the tanner usually receives them.

A duplicate series of strips of fresh skin was fixed in dilute alcohol, in each case, for comparison with those fixed in Erlicki's fluid. Sections from the Erlicki fixer generally showed various details more sharply than those from alcohol alone. All specimens of skin from the unhairing and bating processes were fixed in alcohol in order to avoid possible complications due to the reactions of the Erlicki fixer with the tannery liquors. Samples of air-dry leather were not fixed, but were imbedded in paraffine either directly or after soaking in santalwood oil and then in molten paraffine.

Dehydrating and Imbedding.— All specimens of skin, after fixing, were kept for the stated lengths of time in the following baths:

1	day	50 per cent alcohol
"	"	95 " " "
"	"	absolute alcohol
"	"	fresh absolute alcohol
½	"	alcohol-xylene
"	"	carbol-xylene
"	"	xylene
"	"	fresh xylene
"	"	molten paraffine.

The mixture of alcohol and xylene consisted of equal volumes of the two. The carbol-xylene is known as a clearing agent and has for its object the removal of alcohol from the specimen; it is prepared by mixing 25 cubic centimeters of melted phenol with 75 cubic centimeters of xylene. Very thick specimens had to be left in the molten paraffine for a much longer time, the object of this bath being to replace the

xylene by paraffine. The strips from the paraffine bath were suspended in aluminum beakers, having a capacity of 100 cubic centimeters, and covered with molten paraffine. The beakers were then plunged into cold water and kept there until the paraffine had completely solidified. The beakers were then heated just sufficiently to loosen the paraffine blocks, which were pulled out and cut into the proper size and shape for placing in the microtome.

Sectioning.—Really good work in preparing sections is possible only when the microtome knife is free from nicks and extremely sharp, the sharper the better. The thickness to which it is desirable to cut the sections depends upon the particular part of the skin to be studied. For a general picture of the whole skin, a thickness of 20 microns is satisfactory.

In the sections of skin taken from the unhairing processes, it will be noticed that there would be nothing to hold the loose epidermis and hair in place, if these were not securely fastened to the slide in some way. In order to prevent the loss of important material from the sections, the entire paraffine ribbons from the microtome were fastened to the slides by means of Mayer's albumen fixative. This is made by mixing equal parts of glycerin and well-beaten white of egg, adding 2 per cent of sodium salicylate, and filtering. A tiny drop of this fixative was spread evenly over the middle of a slide with the finger and was then covered with water. A ribbon, containing a section of skin, was then floated onto the water, which was heated over an alcohol lamp carefully so as not to melt the paraffine. This causes the ribbon to spread out flat and it was then worked into place and smoothed out with a camel's-hair brush. Slides prepared in this way were left to dry for at least one day, the sections meanwhile becoming securely fastened. They were then freed from paraffine by flooding the slides with xylene, after which they were washed with absolute alcohol in preparation for staining.

Staining.—Six stains were used in preparing the sections shown in this book, with the exception of those of the human heel and scalp. These two sections were prepared in Professor Bast's laboratory and were stained with Delafield's hematoxylin and eosin. Where an aqueous stain was to be employed, the section was soaked, for several minutes, successively in the following strengths of alcohol: 95 per cent, 75 per cent, 50 per cent, 25 per cent, and then in water. After the staining, it was worked up through the series of solutions of alcohol in the reverse order, finally being rinsed with absolute alcohol. The six stains used were prepared as follows:

(1) Van Heurck's logwood: 6 grams of powdered logwood extract and 18 grams of alum were ground together in a mortar and 300 cubic centimeters of water added slowly. The mixture was then filtered and 20 cubic centimeters of alcohol were added to the filtrate. The solution was kept exposed to air for several weeks, water being added to replace that lost by evaporation. The sections were kept in this stain for 3 minutes, rinsed in tap water until they turned blue, and then passed through the series of alcoholic solutions of increasing

strength. Sections were transferred from the 95-per cent alcohol to the picro-indigo-carmine solution, where this was used for counterstaining. But where the counterstaining was done with bismarck brown, the sections were transferred from the 95-per cent alcohol to a 0.1-per cent solution of HCl in absolute alcohol, where they were kept until they turned pink and no more color was seen to wash away, after which they were rinsed with fresh alcohol and put into the bismarck brown stain.

(2) Friedlander's logwood: 2 grams of powdered logwood extract dissolved in 100 cubic centimeters of alcohol were mixed with 2 grams of alum dissolved in 100 cubic centimeters of water and 100 cubic centimeters of glycerin. This was used like Van Heurck's stain.

(3) Picro-indigo-carmine: To 100 cubic centimeters of 90-per cent alcohol was added 1.0 cubic centimeter of absolute alcohol saturated with picric acid. This solution was then saturated with indigo carmine and allowed to stand with an excess of indigo carmine, with occasional shaking, for several weeks. The decanted solution was used. Sections were kept in this stain from 3 to 4 hours.

(4) Picro-red: 5 cubic centimeters of absolute alcohol saturated with picric acid were added to 55 cubic centimeters of 90-per cent alcohol saturated with the dye Leather Red-X. This solution was diluted with alcohol to 10 times its volume before using. Sections remained in this stain for 2 minutes.

(5) Weigert's resorcin-fuchsin: 2 grams of basic fuchsin and 4 grams of resorcin in 200 cubic centimeters of water were boiled for 10 minutes, 25 cubic centimeters of a 30-per cent solution of ferric chloride were then added and the boiling was continued for 5 minutes. Then a saturated solution of ferric chloride was added until all of the color was precipitated. The mixture was allowed to stand over night to cool and settle and the supernatant liquor was decanted off and discarded. The residue was dissolved in 200 cubic centimeters of boiling 95-per cent alcohol and the hot solution was filtered into a bottle. After it had cooled, 5 cubic centimeters of concentrated HCl were added. For staining, this solution was diluted with an equal volume of alcohol and sections were left in it from 60 to 90 minutes, after which they were rinsed with alcohol.

(6) Daub's bismarck brown: To 95 cubic centimeters of absolute alcohol were added 5 cubic centimeters of saturated lime water and then more bismarck brown than would dissolve and the whole was shaken and allowed to settle, the solution being decanted off after standing for several days. Fifteen cubic centimeters of alcohol were added to the solution to replace any lost by evaporation, which would otherwise cause a precipitation of some of the dye. Sections were kept in this stain for 1 day.

Mounting.—Since the sections of untanned skin were fastened permanently to the slides before staining, the mounting of these was a very simple operation. After the sections were stained, they were rinsed successively with absolute alcohol, alcohol-xylene, carbol-xylene, and xylene. Each section was then covered with a drop of Canada

balsam followed by a cover glass. Sections thus prepared are permanent and ready for study or photographing.

Sections of leather, from the microtome, were uncurled on a piece of smooth paper and fastened by pressing on the paraffine surrounding the sections. They were then removed from the paper in a flattened condition by means of tweezers, dipped into a 1-per cent solution of parlodion in equal volumes of alcohol and ether, and then transferred to slides previously coated with a thin film of santalwood oil. They were carefully smoothed out, covered with santalwood oil, and allowed to stand exposed to air until the alcohol and ether had evaporated, usually about 30 minutes. They were then washed with xylene and covered with balsam and cover glasses. As a rule the staining of leather sections for study is unnecessary, but a stain often assists in getting sharper photographs. Where a stain was employed on leather, the fact is noted under the photomicrograph.

Photographing.—All photographs were taken with a standard type of photomicrographic apparatus. Wratten and Wainright "M" plates were used and developed according to the directions which accompany them. The source of light transmitted through the sections was a 6-volt mazda lamp having a concentrated filament. The light was filtered through appropriate color screens, consisting of the standard Wratten filters. The stains on the sections, together with the color screens, generally furnished all the detail or contrast necessary, but where this was not entirely satisfactory, the plates, after developing, were treated with standard intensifying or reducing agents as needed.

Certain precautions were necessary in photographing grain surfaces for comparison. The hair follicles run obliquely to the surface, in consequence of which the lights and shadows depend upon the angle at which the light strikes the openings of the follicles. This was made uniform for all skins with nearly straight follicles by using for reference the plane including the line of the follicle and intersecting the plane of the grain at right angles. A beam from a powerful arc lying in the plane perpendicular to these two planes was made to strike the grain surface at an angle of 45 degrees.

General.—Halftones were used to reproduce all photomicrographs excepting those in Figs. 20 to 27 inclusive, which were printed from line etchings. Because of the low magnification and consequent fineness of the fibrous tissues, a good reproduction could not be obtained by means of halftones; even a very fine screen produced an appreciable blurring effect. Line etchings, made without a screen, gave a much better result, the resulting increase in sharpness of the fine lines more than compensating for the loss in shading.

All vertical sections are shown with the outer surface of the skin upward. Under each photomicrograph is given the location or region of the body from which the specimen was taken, where this was known, the thickness at which the section was cut in the microtome, the stains applied to the section, the eyepiece, objective, and filter used in photographing, and the final magnification of the section as it appears in the book.

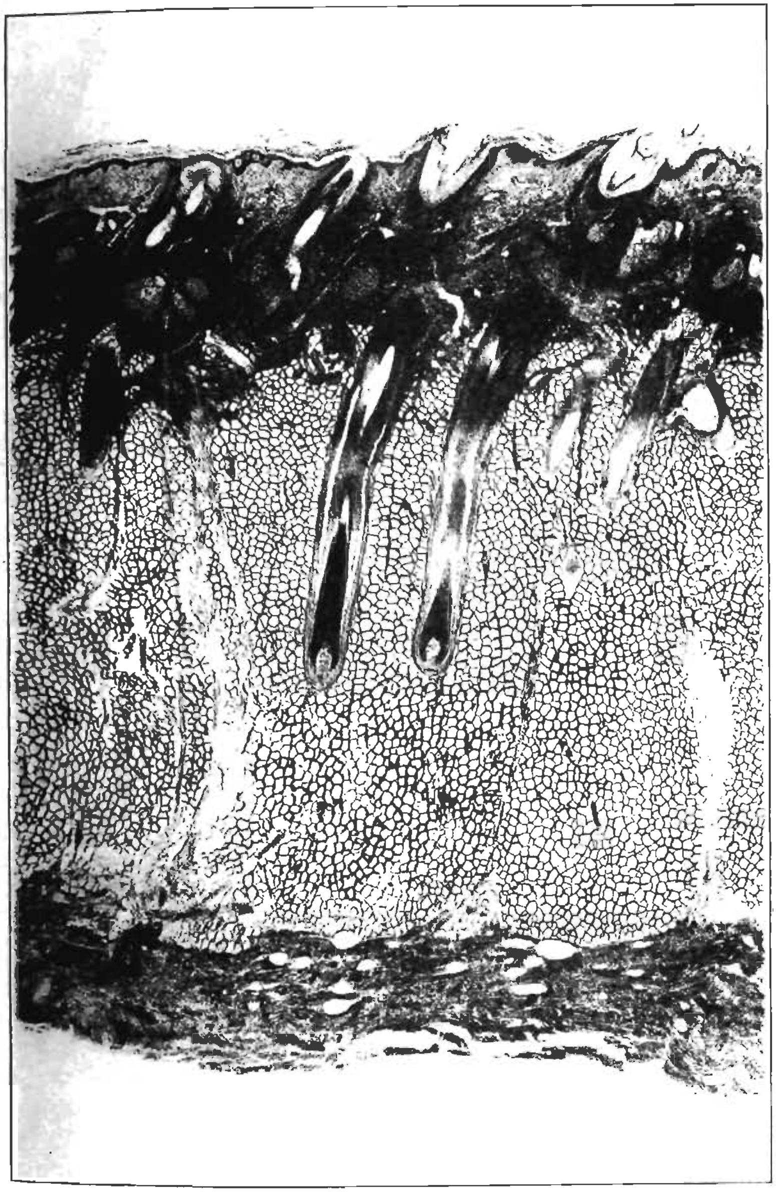

Fig. 1.—Vertical Section of Human Skin.

Location: scalp.
Thickness of section: 20 μ.
Stains: Delafield's hematoxylin, Eosin.

Eyepiece: none.
Objective: 48-mm.
Wratten filter: H blue green.
Magnification: 20 diameters.

Fig. 2.—Vertical Section of Human Skin.

Location: lower part of back.
Thickness of section: 20 μ.
Stains: Van Heurck's logwood, Daub's bismarck brown.

Eyepiece: none.
Objective: 32-mm.
Wratten filter: H-blue green.
Magnification: 32 diameters.

General Histology of Skin.

It is not uncommon to find in the literature descriptions of skin structure that apparently clash. Occasionally an author will present what purports to be a general description, but which is actually based upon the examination of a single type of skin structure. Figs. 1, 2, and 3 all represent vertical sections of human skin, but the first was taken from the scalp, the second from the lower part of the back, and the third from the heel. A detailed description of one would give a very misleading picture of either of the others. In the section from the scalp, fat cells make up the greater portion of the whole, while in that from the back there are relatively very few fat cells, but a great abundance of fibers of connective tissue. In the section from the heel, fat cells and connective tissues are both very prominent, but no hairs are seen. Practically, these sections represent very different types, yet all three conform to a common basic structure. A structure common to all skin may be greatly exaggerated in one type and scarcely detectable in another.

All four general classes of tissues, epithelial, connective, muscular, and nervous, are present in the skin, as well as those of the blood. These tissues either consist of cells or are the product of cells. The epithelial tissues consist of layers of cells, which cover all the free surfaces of the animal body. The connective tissues are distinguished from the other fundamental tissues of the body by the fact that their cells lie imbedded in extracellular material which appears to be the result of their activity. The various types of connective tissues are distinguished among themselves by the kind of extracellular tissue which they produce, such as bone, cartilage, etc. The muscular tissues have a well developed power of contracting, apparently without change of volume, the decrease in length being compensated by an increase in diameter. The cells of the striated or involuntary muscles are long in relation to their width and are marked with transverse bands, while those of the nonstriated or involuntary muscles are spindle shaped, without transverse striations. The nervous tissue found in the skin is a protoplasmic prolongation of cells lying in the central nervous system, or in the ganglia closely associated with that system.

The skin is divided sharply into two layers, distinct both in structure and origin: a relatively very thin outer layer of epithelial tissue, the epidermis, and a much thicker layer of connective and other tissues, the derma. Raw skin, as an article of commerce, has also a third layer, the superficial fascia, known to the tanner as the adipose tissue or, more commonly, the flesh. In keeping with the nomenclature of the leather trade, the word flesh will be used only in this connection, although in anatomy flesh really means muscle tissue. In life, the adipose tissue, or flesh, connects the skin proper very loosely to the underlying parts of the body. The derma lies between the epidermis and adipose tissue.

In the preparation of skin for tanning, except in special cases, such as the tanning of fur skins, the adipose tissue and the entire

Fig. 3.—Vertical Section of Human Skin.

Location: heel.
Thickness of section: 30 μ.
Stains: Delafield's hematoxylin, Eosin.
Eyepiece: none.
Objective: 48-mm.
Wratten filter: H-blue green.
Magnification: 20 diameters.

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epidermal system must be removed intelligently and with extreme care, leaving the derma to be converted into leather. The epidermal system, adipose tissue, and derma will be described in turn.

The epidermis is made up of a cellular strata originating from the ectoderm, the outer layer of the young embryo, and independently of the derma, which is derived from the mesoderm, or middle layer. These two layers grow independently throughout life and differ materially in both chemical and physical properties. In Fig. 2 the epidermis can be seen as a dark band forming the upper boundary of the skin and constituting only about 1 per cent of the total thickness. So far as its growth is concerned, the epidermis may be looked upon as a parasite, although it is a most important part of the body. It has no blood vessels of its own, but rests upon the upper surface of the derma and draws its nourishment from blood and lymph supplied by the blood vessels of the derma. It grows only through the reproduction of its own cells.

The portion of epidermis in contact with the derma is a layer of living epithelial cells, rather elongated in shape. It may be mentioned that a cell consists of a nucleus suspended in protoplasm enclosed between very thin walls acting as a semi-permeable membrane. Nourishment from the lymph and blood streams diffuses through the cell walls, and after a certain period of growth the cell divides mitotically, forming two cells. This change appears to be initiated by the nucleus. In the deepest layer of the epidermis, each cell increases in height and then subdivides, forming two cells, one above the other. This process is repeated indefinitely. As the older cells are pushed outward, they become flattened by dehydration and other changes. During this process, the protoplasm dries up and the cells lose their power of reproduction. In the outermost layer, the cells are very dry and scaly and are gradually worn away. This scaling is often very noticeable on the scalp in the form of dandruff, which, in itself, is not the result of a disease, but rather is evidence that the epidermal cells are functioning and reproducing vigorously.

Where the epidermis is very thick, as on the heel, the gradual transition which the cells undergo in their outward course gives the epidermis the appearance of having several distinct layers. The portion of the epidermis shown in the upper left hand corner of Fig. 3 is shown at a very much higher magnification in Fig. 4. Now the several strata can be seen very plainly.

The layer marked E is the uppermost part of the derma and numerous protuberances of its surface, called papillæ, can be seen extending upward into the epidermis, giving the boundary between epidermis and derma a serrated appearance. D is the Malpighian layer of the epidermis, or *stratum mucosum*. It is built up of several rows of living epithelial cells, whose nuclei appear in the picture as dark spots or rods. Tiny fibers, often called prickles, pass from cell to cell, holding them together and securing them to the derma. Extending between these prickles, which look as if they were walls in section, are protoplasmic processes and it is supposed that food passes upward

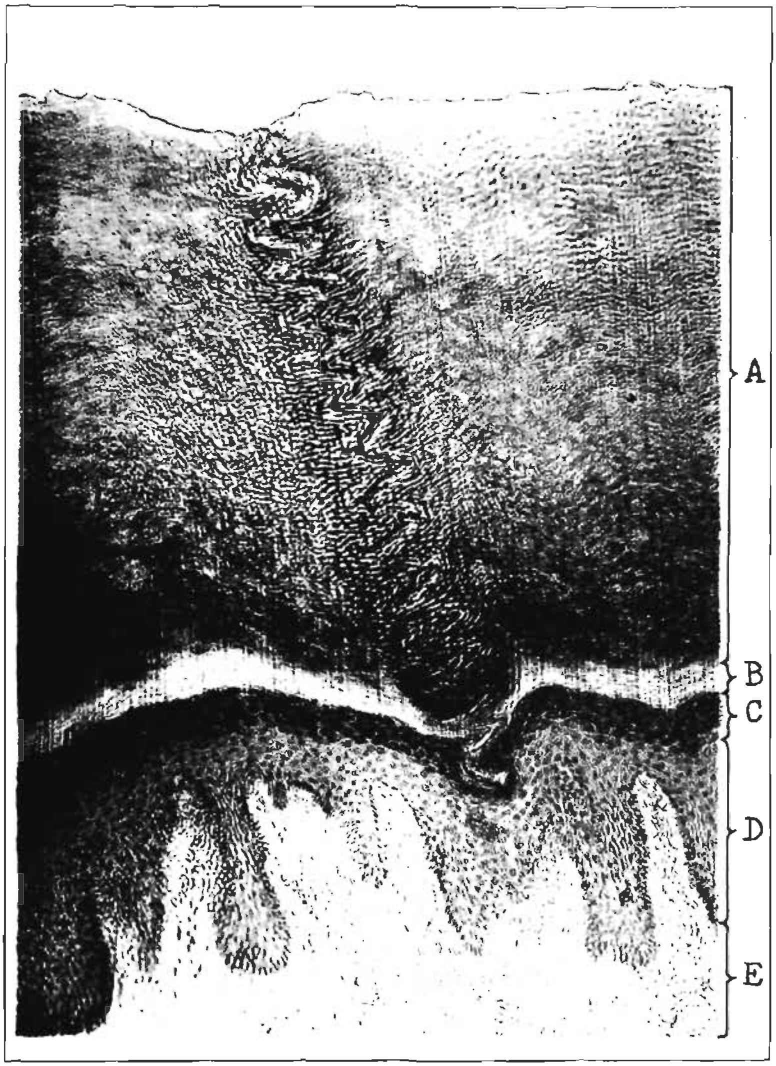


Fig 4.—Vertical Section of Human Epidermis.

A. Stratum corneum.
B. Stratum lucidum.
C. Stratum granulosum.
D. Stratum mucosum.
E. Pars papillaris.

Location: heel.
Thickness of section: 30 μ.
Stains: Delafield's hematoxylin, Eosin.

Eyepiece: none.
Objective: 8-mm.
Wratten filter: A-red.
Magnification: 100 diameters.

between the cells and waste from the upper layers downward. From this food the cells derive the nourishment necessary for reproduction. This layer contains no blood vessels, but very fine nerve fibers pass from the derma into this layer, forming a network between the cells and terminating in bulbous swellings or undergoing a gradual breaking up into nerve granules.

As the new cells are formed, the older ones are pushed outward where nourishment is no longer available and the protoplasm of the cells gradually dries up. Upon staining, the cells then appear as though they contained coarse granules and form the layer shown at C, which, from its appearance, has been called the *stratum granulosum*. The cells also contain a pigment, which is at least partly responsible for the color of the skin. This pigment, known as melanin, is thought to be a derivative of hematin containing iron and sulfur. It is very concentrated in the skin of the negro and almost entirely absent from the skin of a blonde. Apparently the pigment is formed as a protection against strong sunlight, both for the skin and the underlying tissues. The pigmented layer may thus be looked upon as a color filter. When the pigment-containing cells are collected in spots, they appear as freckles. The pigment in the negro skin is found in the deepest cells of the *stratum mucosum*, in the connective tissue cells of the upper part of the derma, and in the wandering cells of the lymph, found in the lymph spaces or between the cells of the epidermis or connective tissues. The pigment granules are found only in cells.

As the cells are pushed still further outward, the cell granules break down, yielding a material, called eleidin, which resists staining and gives the epidermis in this region a transparent appearance, from which it has derived the name *stratum lucidum*. This layer is shown at B.

The cells continue to undergo changes during their outward course, becoming drier and flatter, and finally form the very thick layer shown at A, the *stratum corneum*, in which the cells tend to break away from each other and to scale off. This layer is being worn away continually and is replaced by the newer cells from below. The corneous layer is a very poor conductor of heat and the waxy material usually present on its surface makes it water repellent. In the photomicrograph a duct can be seen taking a spiral course up through the corneous layer. This is the outlet of a sudoriferous or sweat gland seated in the derma. Its opening at the surface of the corneous layer is called a pore.

All of the strata noted above can be detected only where the epidermis is very thick. Elsewhere only the *stratum mucosum* and *stratum corneum* are visible. In no case have we yet observed a section of skin used for making leather where more than these two layers could be recognized in the epidermis.

The independent growth of the epidermis and derma involves a number of important appendages of the skin. In the epidermal system, the reproduction of epithelial cells produces, not only the epidermis, but also the hair and the sebaceous and sudoriferous glands. These cellular structures are composed of proteins of the class known

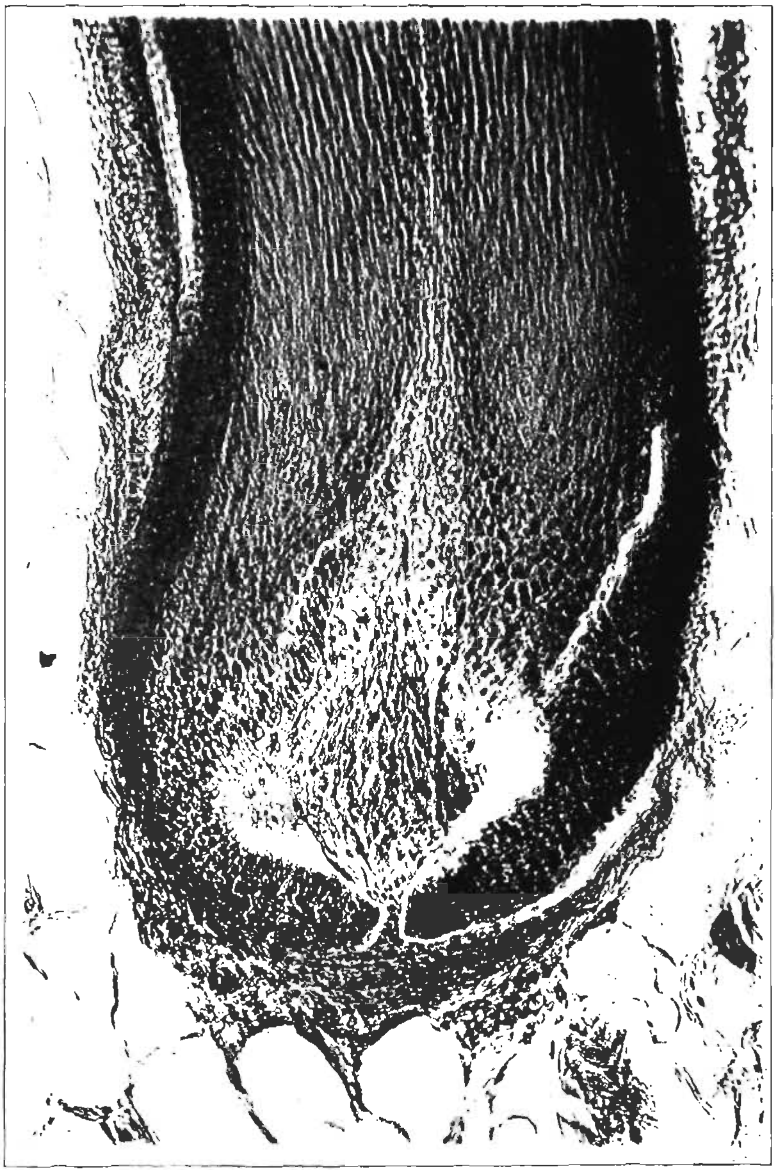


Fig. 5.—Vertical Section of Hair Bulb from Hog, *in situ*.

Location: butt.
Thickness of section: 20 μ.
Stains: Van Heurck's logwood, Picro-indigo-carmine.

Eyepiece: 5X.
Objective: 8-mm.
Wratten filter: F red.
Magnification: 225 diameters.

as keratins as distinct from the collagens and elastins of the derma. Where a portion of the epidermis is lost, through accident, it can be regenerated only by the surrounding epithelial cells spreading over the bare spot, by reproduction. The necessity for removing the epidermal system completely before tanning and without any injury to the derma makes the difference in chemical composition between the two systems a matter of great importance to the tanner.

In the class with hair belong also nails, claws, hoofs, scales, and feathers, which are all special growths of the epidermis. To the naked eye, the hair appears to pierce the skin, but actually it does not do so. An examination of Fig. 2 will show that the epidermis dips down into the body of the derma, forming a pocket, or follicle, in which the hair grows. The follicle is complex in structure because it is made up of the epidermal layers on the hair side and of the layers of the derma on the other. At its bottom, the follicle is penetrated by a projection coming from the derma and known as the hair papilla, which is supplied with both nerves and blood vessels.

A good example of a hair papilla is shown in Fig. 5 in the hair bulb from the skin of a hog. The bottom end of the bulb appears like a pair of pincers with the jaws slightly open and facing downward. A similar structure may be seen in the hair bulbs of the scalp shown in Fig. 1. Passing through the opening in the jaws into the large open space above and resembling a candle flame in shape is the papilla, which contains tiny nerves and blood vessels which supply nourishment. Lining the lymph space surrounding the papilla are numerous epithelial cells, which derive from the blood and lymph the nourishment necessary for reproduction. As new cells are formed, the older ones are pushed outward through the follicle, forming the hair. The rate of growth of the hair is determined by the rate at which the cells surrounding the papilla reproduce.

The newly formed cells of the hair, like those of the Malpighian layer of the epidermis, are very soft. As they are pushed upward, they become elongated in shape and harder. In forming the hair, they assume the shape of the follicle; if this happens to be curved, the hair will be curly. In the negro, the follicles often have a curvature of nearly 90 degrees, which accounts for the tightness of the curls.

The portion of the hair showing above the surface of the skin is called the shaft and the lower portion the root, which enlarges into a bulb at its lower extremity, where it is penetrated by the hair papilla. The shaft is made up of a central medulla, or pith, of rounded cells, containing eleidin granules, surrounded by a much thicker portion composed of long fibrillated cells, containing pigment, and enclosed by an outer layer of cells which become hardened in the form of overlapping scales. These scales, which give fur and wool their felting properties, open outward so as to resist the pulling out of the hair. Unless the lighting is properly adjusted and the magnification sufficiently great, the scales are not easily discernible. In Fig. 6 may be seen the scales of a tiny piece of wool. The scales of one side and the shadows of those on the other both show because the wool

Fig. 6.—Segment of Sheep Wool.

Stain: none.
Eyepiece: 7.5X.
Objective: 4-mm.
Wratten filter: H-blue green.
Magnification: 1260 diameters.

was photographed with transmitted light. The same general structure can be seen on most hair, but it is not always so pronounced.

When a hair is shed, after reaching the limit of its existence, the epithelial cells left surrounding the hair papilla keep on multiplying and soon another hair is formed to replace the one shed. Baldness results from the failure of the blood vessels of the papilla to furnish the required nourishment or from the destruction of the epithelial cells in some other way. Any serious attempt to grow hair on a bald head must be accompanied by some means of introducing living epithelial cells into the hair follicles, of which there are something like a thousand to the square inch. In other words, we cannot grow a crop without seeds or seedlings.

In old age, pigment is no longer available for the hair cells and the new hairs, containing no pigment, appear gray in color. Hair containing pigment, however, may look white by reflected light, due to the presence of tiny air bubbles among the cells.

Each hair follicle is supplied with sebaceous glands with ducts emptying into the upper portion of the follicle. A group of these glands can be seen in Fig. 2. They are lined with epithelial cells which secrete from the blood the materials required for the synthesis of the oils which they produce. When they become charged with oil, the protoplasm disappears and the cell breaks down, discharging the oil into the duct. New cells are continually being formed to replace the old ones. The oil is forced into the follicle, where it coats and lubricates the hair, and finally to the surface of the skin, which it softens and protects against the cold. In contact with air, this oil thickens to the consistency of ear wax, to which it is related. When the ducts become clogged with dirt, the pressure behind them causes them to become distended, giving rise to blackheads. Sebaceous glands are sometimes found also in parts of the skin free from hair.

Attached to each hair follicle, just below the sebaceous glands, and extending obliquely upward through the derma, almost to the surface, is a bundle of nonstriated muscle tissue, known as the erector pili muscle. In Fig. 2 one of these muscles forms a V with the hair follicle, and the sebaceous glands may be seen within the angle so formed. The nerves supplying these muscles are known as the pilomotor nerves. These muscles contract under the influence of emotions, such as fear, surprise, anger, or other disagreeable states, or in response to cold or grazing tactile stimuli. Among the commoner visible effects are the roughening of the skin called goose-flesh and the effect of the hair standing on end, very pronounced in a frightened cat.

The real purpose of the erector pili muscles is apparently to protect the body against sudden changes of temperature by their control over the operation of the glands; they seem to act as effectively as a thermocouple in a good thermostat. Their contraction puts a pressure on the glands which causes the cells to give up their oil to the hair follicle and, in the process, the cells are destroyed. The oil is then forced up through the follicle to the surface of the skin, where

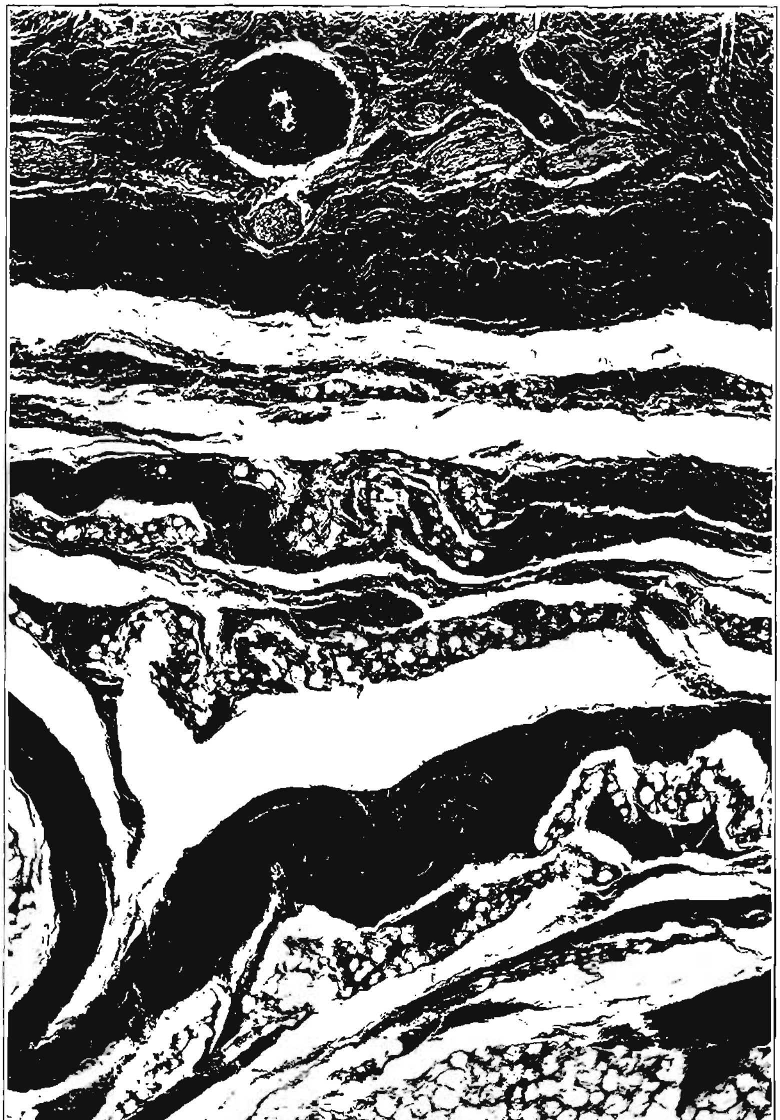


Fig 7.—Vertical Section of Calf Adipose Tissue.

Location: butt.
Thickness of section: 20 μ.
Stains: Van Heurck's logwood, Daub's bismarck brown.

Eyepiece: none.
Objective: 16-mm.
Wratten filter: H-blue green.
Magnification: 70 diameters.

it tends to stop the action of the sudoriferous glands and the evaporation of water from the surface of the skin.

The sudoriferous or sweat glands are coiled sacs with spiral ducts leading to the surface of the skin. In Fig. 3 several of these ducts can be seen winding up through the epidermis and terminating at the surface as pores. Often the ducts seem to lead into the hair follicles above the openings of the ducts of the sebaceous glands. The sacs of the sweat glands are lined with epithelial cells, which are continuous with the cells of the Malpighian layer of the epidermis, and which secrete water, salts, urea, and other wastes from the blood and pass them out through the ducts. Where no sebaceous glands are present, the sudoriferous glands also provide an oily fluid to keep the surface of the skin soft. These glands serve the dual purpose of disposing of waste products and of permitting control of the body temperature through the regulation of the rate of evaporation of water.

This entire epidermal system, including the epidermis, hair, and sebaceous and sudoriferous glands, must be removed from the skin in such manner that the derma suffers no injury that can be detected in the finished leather.

The skin is connected to the underlying parts of the body very loosely by means of fibers of connective tissue, usually called adipose tissue because it is so frequently the seat of fat deposits, most numerous in the vicinity of the abdomen, which serve to protect the body against cold. The looseness of connection allows the skin very free movement and, incidentally, makes flaying a much simpler matter than it would otherwise be. The adipose tissue, while not a part of the skin proper, is of importance to the tanner because much of it remains adhering to the skins received at the tannery and must be removed prior to tanning. If left on the skins, it greatly impedes the progress of tanning.

In Fig. 7 is shown a vertical section of adipose tissue from the butt of a calf skin along with the lower portion of the derma. The top quarter of the picture shows a portion of derma bound on its under side by strands of elastin fibers, appearing as compact masses of black threads; actually they are of a pale yellow color. The fat cells of the adipose tissue are arranged in layers and are held together by fibers of connective tissue. The light colored tissues are the white fibers, composed of collagen, and the dark ones are the yellow fibers of elastin. Large arteries, nerves, and veins which supply the derma traverse the adipose tissue in many places and can often be seen heavily protected with connective tissue. This region is sometimes supplied also with striated muscle fibers to permit the voluntary twitching of the skin.

The removal of the adipose tissue of the skin, preparatory to tanning, is an operation known as fleshing. This is done efficiently when all of the tissues underlying the derma are cut away, leaving the derma itself entirely intact.

It is the derma, or true skin, that is actually used to make leather

Fig. 8.—Vertical Section of Reticular Layer of Calf Skin.

Location: butt.
Thickness of section: 20 μ.
Stains: Van Heurck's logwood, Daub's bismarck brown.

Eyepiece: 5X.
Objective: 16-mm.
Wratten filter: B-green.
Magnification: 170 diameters.

and the chief leather-forming constituent of the derma is collagen, the substance of the white fibers of connective tissue. Sound leather can be produced only from skins in which these fibers are well developed and abundant. The three contrasting structures in Figs. 1, 2, and 3 are typical of the extremes found in the skins of the lower animals. A skin composed chiefly of fat cells is of little value in making leather and one in which large groups of fat cells are interspersed between the collagen fibers will yield only a spongy leather because of the empty spaces left after the fat cells have been destroyed in the processes preparatory to tanning. The tendency toward one extreme or the other depends largely upon the habits and feeding of the animal as well as upon its species. In considering the general structure of skin, one should look upon the major portion of the derma as consisting of both fat cells and connective tissues, either of which may be very abundant or relatively scarce.

Unlike the epithelial tissues, the major portion of the connective tissues is not made up of cells, but results from the activity of migratory cells very much smaller in size than the extracellular material. The relation of these cells to the collagen fibers of calf skin can be seen in Fig. 8. The cells stain more deeply than the fibers and appear in the picture as black specks having a diameter of about 1 millimeter, which means that the actual cells have a diameter of about 1/170th of this. In the sections we have examined, the abundance of these cells diminishes with increasing age of the animal.

By examining the cross sections of fibers running perpendicular to the plane of the page, the arrangement of the fibers, or fibrils, in bundles can be seen very plainly. Seymour-Jones regards the fibers as enclosed in very thin sheaths of what he terms "fiber sarcolemma." While we have not been able, as yet, to detect such a sheath microscopically, the investigations of Wilson and Gallun, described in Chapter 8, seem to indicate that the surfaces of the collagen fibers are very much more resistant to tryptic digestion than the material just under the surface.

Of the two kinds of fibers composing the connective tissues, the collagen fibers are very much thicker and more abundant than the elastin fibers. There is usually a dense layer of elastin fibers at the lower surface of the derma, where it is attached to the adipose tissue, as shown in Fig. 7, and another in the region of the erector pili muscles. But the greater portion of the derma seems to contain relatively few elastin fibers and these are generally to be found surrounding the blood vessels and nerves traversing the derma.

The main trunk lines of blood vessels and nerves supplying the derma run parallel to the surface just above the lower elastin layer. From these trunk lines branches shoot upward and are distributed to all parts of the derma. A network of lymph ducts also is distributed throughout the skin.

Cross sections of the arteries and veins show three distinct layers: an outer layer of collagen and elastin fibers, a middle layer of non-striated muscle tissue and elastin fibers, and an inner membrane of

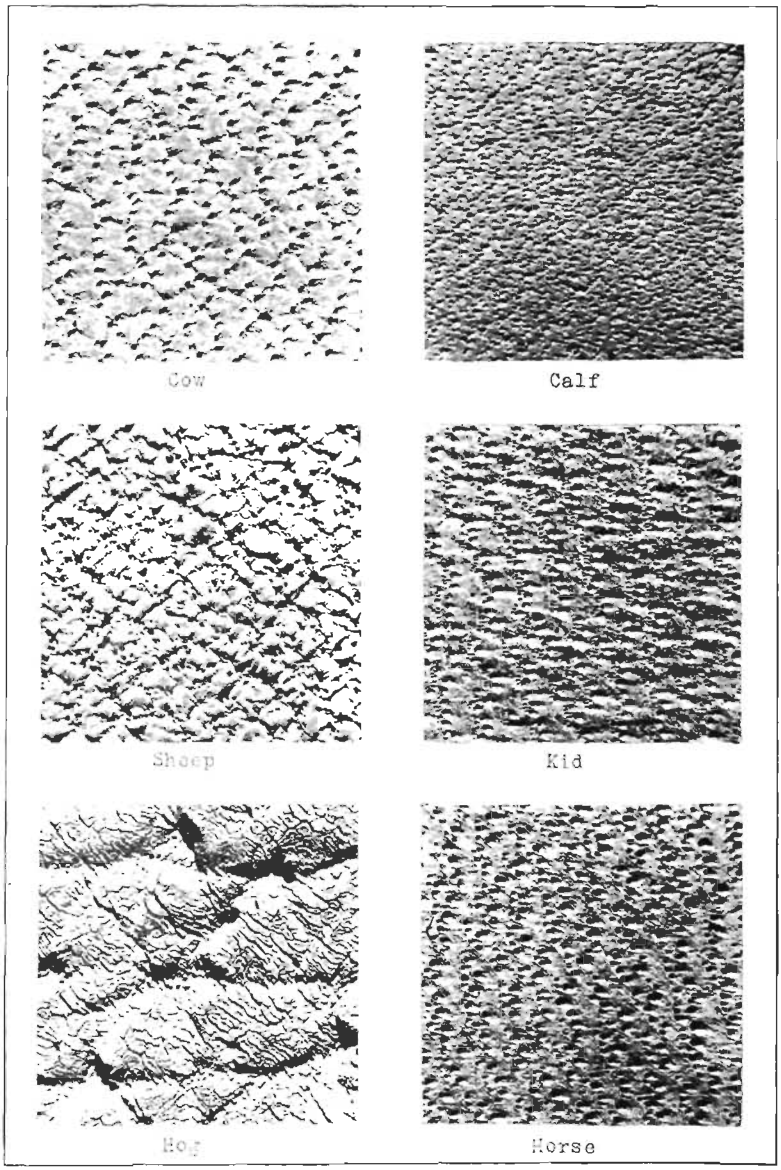


Fig. 9.—Grain Surfaces of Tanned Skins.

Eyepiece: none.
Objective: 48 mm.
Wratten filter: K2-yellow.
Magnification: 7 diameters.

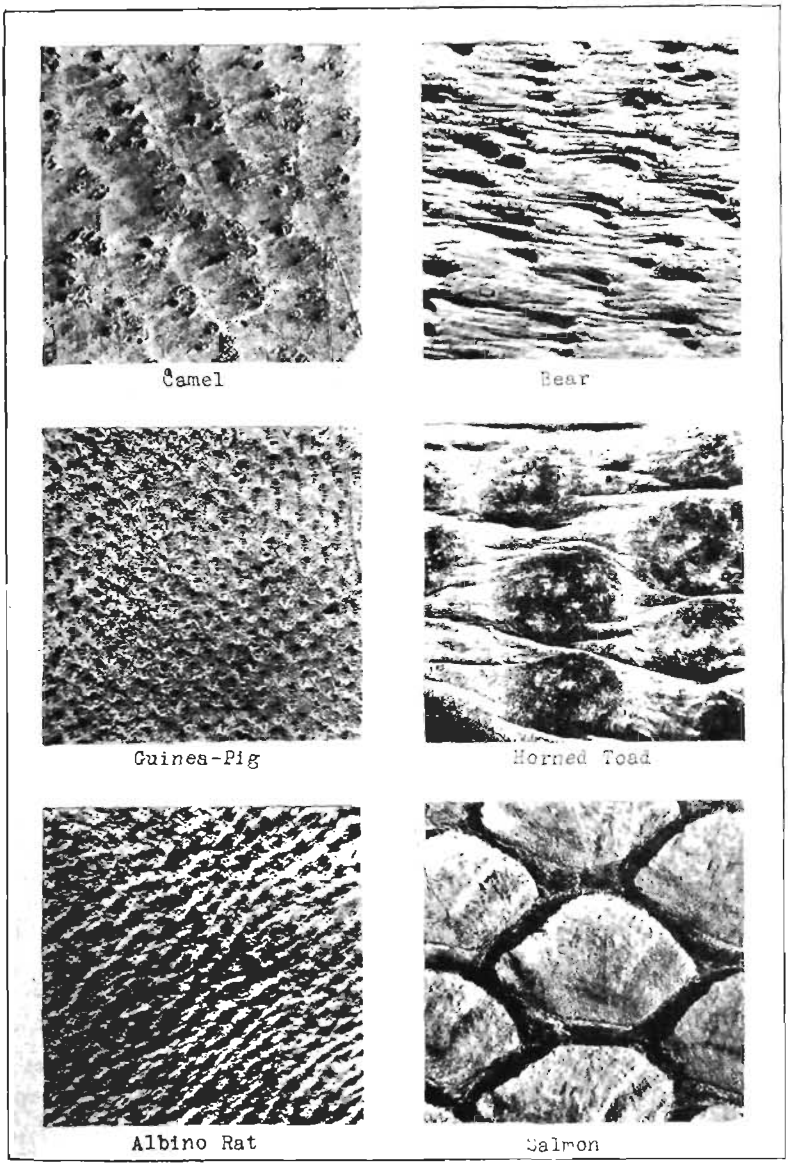


Fig. 10.—Grain Surfaces of Tanned Skins.

Eyepiece: none.
Objective: 48-mm.
Wratten filter: K2-yellow.
Magnification: 7 diameters.

flattened cells. All three layers are pronounced in the arteries, but in the veins the outer layer is very much thicker than the inner layers, which are much less developed and collapse when the vein is empty. The veins are also equipped with semilunar valves in order to prevent backflows of blood.

A cross section of an artery can be seen at the top of Fig. 7. It is the large circular body just to the left of the midline. To the right of the artery is a vein, which has collapsed. The circular mass just under the artery is a cross section of a bundle of nerves. Three more sections of nerve bundles are prominent, elongated in shape, two just below the vein and one to the extreme left of the artery.

In those parts of the body where the sense of touch is well developed, as in the fingers, there are numerous protuberances of the surface of the derma into the epidermis, called papillæ. These are very pronounced in the section of skin from the human heel shown in Fig. 3. They are arranged in definite patterns which do not change throughout life. The design of the thumb print is produced by the papillæ. They seem to be absent entirely from some parts of the body, particularly where the sense of touch is not well developed and where the epidermis is very thin. They are of two kinds, one containing blood vessels furnishing lymph to the active epithelial cells in their vicinity and the other containing the nerves sensitive to touch, pain, heat and cold. The epidermis above the papillæ is thinner than at other points, the papillæ serving the purpose of bringing the nerve ends nearer to those surfaces where they are most needed.

The portion of the derma immediately in contact with the epidermis has been called the "grain membrane" by Seymour-Jones because it forms the grain surface of the finished leather. Although its boundary on the side in contact with the epidermis is very sharp, on the other side it blends into the rest of the derma with no sharp change of properties. The fibers of connective tissue grow finer as they near the grain surface, in which the fibers are extremely fine and generally run parallel to the surface. They can be seen very plainly in the horizontal section of tanned calf skin shown in Fig. 150, of Chapter 16. Whether or not the fibers of the grain surface are continuous with those of the connective tissues of the derma, they seem to possess somewhat different properties. When unhaired skin is kept in boiling water, the fibers of the grain surface remain as a thin sheet, although somewhat changed, long after the larger collagen fibers below have passed into solution as gelatin. The outer surface is then very sharp, but the inner side, facing the remnants of the collagen fibers, appears jellylike and heterogeneous, indicating a gradual change in properties of the fibers as they pass from the derma into the grain surface.

It is of great importance that no damage be done to the grain surface in removing the epidermis, because it determines the appearance of the finished leather. It is therefore fortunate for the tanner that the fibers in this surface are more resistant to the action of alkalies than the epidermis above it and more resistant to the action of tryptic enzymes than the elastin fibers below it. The grain surface

is readily attacked by proteolytic bacteria under certain conditions, however, resulting in what is known to the tanner as pitted grain.

The design of the grain surface, as seen on the skin after unhairing and tanning, is distinct for each species of animal, while the fineness of the pattern is an indication of the age of the animal. It is due to the arrangement of the hair follicles and pores, and of the papillæ where these are present. The grain surfaces of the tanned skins of a number of different animals are shown in Figs. 9 and 10. They are all magnified to exactly the same extent and are directly comparable. It will be noted that the cow and calf have the same pattern, but that it is much coarser in the older animal. These designs can be used to identify different species of animal.

We shall now turn from considering the general histology of skin to the more detailed structures shown by definite types of skins used in making leather.

Cow Hide.

In selecting skin for the production of heavy, sound and durable leather, the tanner usually chooses the hide of the steer or cow. In Fig. 11 is shown a vertical section of cow hide taken from the thickest part of the butt. The specimen was fixed in Erlicki's fluid immediately after the death of the animal. This is the type of skin suitable for manufacture into sole leather or heavy belting or harness leather. Over 80 per cent of the total thickness of the hide is made up of heavy, interlacing bundles of collagen fibers, the chief leather-forming constituent of skin, and very few of the fat cells that tend to make the leather spongy are to be found among these fibers.

The epidermis appears as a thin, dark line forming the upper boundary of the section and occupying barely one-half of one per cent of the total thickness, the rest being the derma, the adipose tissue having been removed from this portion of the hide in flaying. The epidermis can be seen to dip down into the derma in many places, forming the follicles in which the hairs grow.

The presence of the muscles, glands and follicles in the top fifth of the derma give this region the appearance of a layer quite distinct from the lower part of the derma. Indeed, it is advantageous, in leather manufacture, to look upon the derma as divided into two distinct layers. The dividing line might conveniently be taken as that formed by the deepest points of the sudoriferous, or sweat, glands. The lower, fibrous region of the skin is often referred to as the reticular layer because of the network appearance of the collagen fibers. This name might well be accepted for most skins suitable for leather manufacture, although it might seem somewhat strained for skins in which the derma is made up largely of fat cells. The chief function of the upper layer seems to be that of a thermostat for the body and the writer, therefore, proposes the name thermostat layer as indicating its structure as well as its chief function.

In Fig. 11 the thermostat layer occupies the top fifth and the

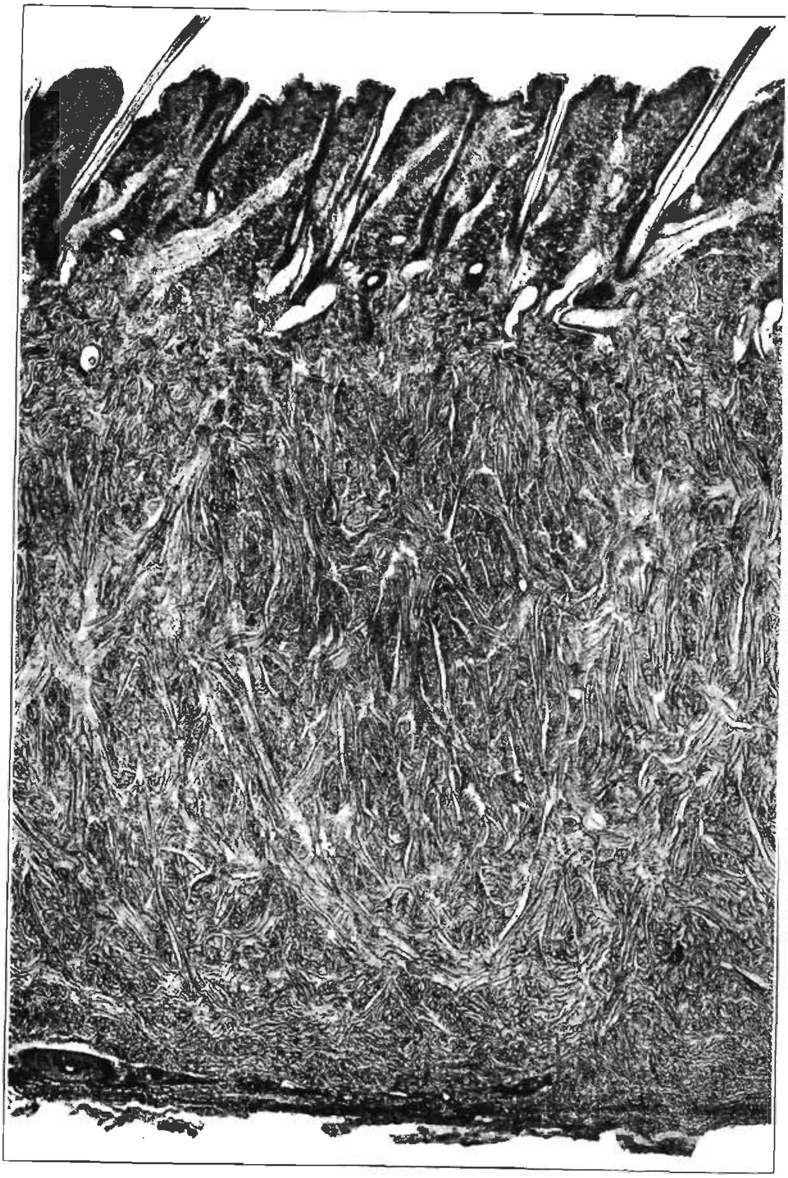


Fig. 11.—Vertical Section of Cow Hide.

Location: butt.
Thickness of section: 20 μ.
Stains: Van Heurck's logwood, Daub's bismarck brown.
Eyepiece: none.
Objective: 48-mm.
Wratten filter: F-red.
Magnification: 19 diameters.

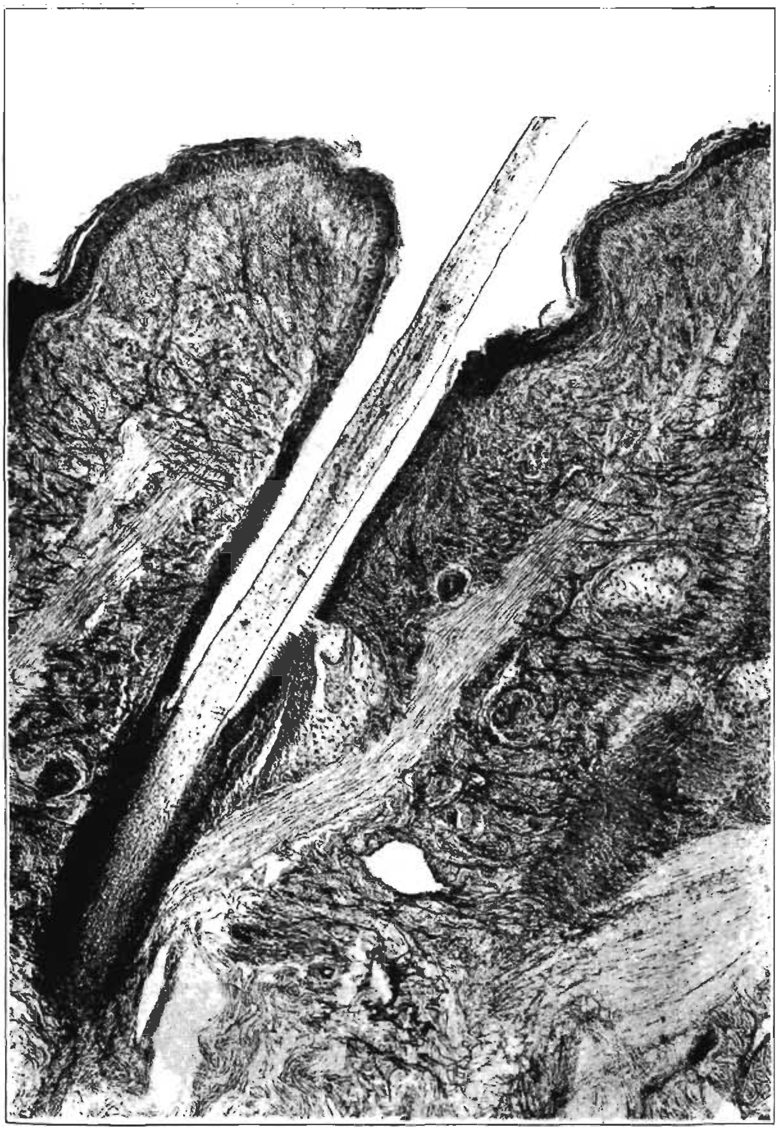


Fig. 12.—Vertical Section of Thermostat Layer of Cow Hide.

Location: butt.
Thickness of section: 20 μ.
Stains: Van Heurck's logwood, Daub's bismarck brown.

Eyepiece: 5X.
Objective: 16-mm.
Wratten filter: H-blue green.
Magnification: 85 diameters.

reticular layer the remaining four-fifths of the section. The advantage of dealing with these layers separately is made clear by the fact that the structure of the reticular layer determines the physical properties of the leather such as tensile strength, solidity, resilience, etc., while the thermostat layer determines more particularly the appearance of the leather. In making the finer grades of leather, a great deal of attention must be paid to the thermostat layer. It is a matter of considerable importance that this layer is almost as thick in a small skin as in a large one; in the thinner skins and even in the thinner parts of the same skin, this layer occupies a greater proportion of the total thickness.

The section in Fig. 11 is magnified only 19 diameters. In order to show the structure of the thermostat layer in greater detail, the upper left hand corner of this section was magnified to 85 diameters. At this greater magnification, it is shown in Fig. 12. The Malpighian and corneous layers of the epidermis can now be clearly differentiated, the latter becoming extremely thin where it lines the hair follicle. The *stratum granulosum* and *stratum lucidum* do not appear to be present in the epidermis. Attached to the base of the hair follicle and weaving its way upward to the right is the erector pili muscle. Just above this muscle and emptying into the hair follicle is a group of sebaceous glands. The empty space near the lower left hand corner is that formerly occupied by a sweat gland whose duct has wandered out of the plane of the section, reappearing as a pore to the right of the hair just at the entrance to the hair follicle. The fine, black, threadlike lines running roughly parallel to the surface and to be found throughout the thermostat layer are the elastin fibers, or yellow fibers of connective tissue. In this layer, the collagen fibers are very much finer than in the reticular layer and appear to be broken up into individual fibrils. The grain surface appears only as portions of tiny fibrils with no sharp line of division from the rest of the derma. No papillæ are to be seen in this section; in fact, we found no papillæ in any part of the cow hide, except in the region of the legs.

In order to present a still clearer picture of the important thermostat layer, we prepared series of sections parallel to the surface of the hide. Strips of hide imbedded in paraffine were placed in the microtome and sections, each 20 microns thick, were cut in succession from the corneous layer to a point in the reticular layer, every section being kept in order and mounted. The five horizontal sections shown in Figs. 13 to 17 were prepared from a strip of hide taken from the thigh so as to include the papillæ, which were not present in the other regions. Fig. 13 is a section cut through the epidermis. In the center is the opening of a hair follicle. The circular mass just above the center is the cross section of a hair. The stringy lines forming an oval shaped mass about the hair are the part of the corneous layer of the epidermis which dips down into the hair follicle. The heavy dots seen throughout the rest of the picture are the nuclei of the cells of the Malpighian layer of the epidermis. The irregularly shaped, light-colored patches are cross sections of the papillæ of the derma

Fig 13.—Horizontal Section of Cow Hide.
(Through epidermis.)

Location: thigh.
Thickness of section: 20 μ.
Stains: Van Heurck's logwood, Daub's bismarck brown.
Eyepiece: 5X.
Objective: 8-mm.
Wratten filter: H-blue green.
Magnification: 200 diameters.

which protrude into the epidermis and are made up chiefly of nerves and blood vessels.

Fig. 14 represents a section cut 0.30 millimeter below the upper surface of the corneous layer. It marks the plane of the derma where the ducts of the sebaceous glands empty into the hair follicles. In

Fig. 13.—Horizontal Section of Cow Hide.
(0.30 mm. below upper surface.)

Location: thigh.	Eyepiece: 5X.
Thickness of section: 20 μ.	Objective: 8-mm.
Stains: Van Heurck's logwood, Daub's bismarck brown.	Wratten filter: H-blue green.
	Magnification: 200 diameters.

the lower part of the middle of the picture can be seen the cross section of a hair and of two ducts emptying into the follicle, just above the hair, to right and left. Both the ducts and the follicle are lined with epithelial cells which are continuous with the Malpighian layer of the epidermis and of which they are appendages. The dark, thread-

Fig. 15.—Horizontal Section of Cow Hide.
(0.54 mm. below upper surface.)

Location: thigh.
Thickness of section: 20 μ.
Stains: Van Heurck's logwood, Daub's bismarck brown.
Eyepiece: 5X.
Objective: 8-mm.
Wratten filter: H-blue green.
Magnification: 200 diameters.

like structures are elastin fibers. The tiny collagen fibers of this region, being stained more lightly, are not prominent.

The section in Fig. 15 forms the plane 0.24 millimeter below that of Fig. 14. The hair whose cross section is shown in the lower part of the middle of Fig. 15 is the same as that shown in Fig. 14. The

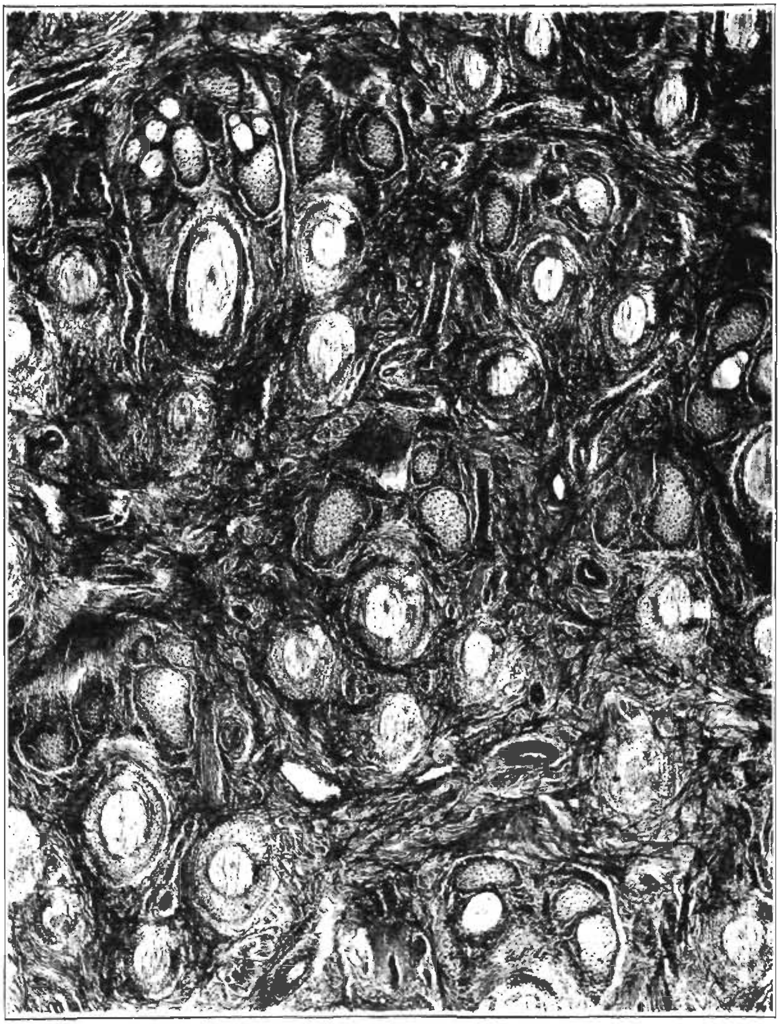


Fig. 16.—Horizontal Section of Cow Hide.
(0.54 mm. below upper surface.)

Location: thigh.
Thickness of section: 20 μ.
Stains: Van Heurck's logwood.
Daub's bismarck brown.

Eyepiece: none.
Objective: 16-mm.
Wratten filter: H blue green.
Magnification: 48 diameters.

hair follicle at this point has a much thicker wall of epithelial tissues and is more thickly bound by elastin fibers. Above the follicle, to the right and left, are the two groups of sebaceous glands whose ducts can be seen emptying into the follicle in Fig. 14. These glands resemble bunches of grapes. Each dot is a cell nucleus and the fine

Fig. 17.—Horizontal Section of Cow Hide.
(0.84 mm. below upper surface.)

Location: thigh.
Thickness of section: 20 μ.
Stains: Van Heurck's logwood, Daub's bismarck brown.

Eyepiece: 5X.
Objective: 8-mm.
Wratten filter: H-blue green.
Magnification: 200 diameters.

lines are the thin walls bounding the cells. A portion of the erector pili muscle is visible at the midpoint of the top of the picture. It is passing obliquely upward through the plane of the section and away from the hair follicle. The contraction of this muscle exerts a pressure upon the cells and their oily contents are forced up through the ducts

and into the hair follicles at the openings shown in Fig. 14. Between the two groups of glands and the hair follicles is a mass of muscle tissue of the same kind as that constituting the erector pili muscle. Apparently the muscle extends also into this region and exerts its pressure upon the cells by a sort of pinching action.

Fig. 16 is a photomicrograph of this section taken at lower magnification so as to show the general arrangement of follicles and glands. The portion appearing in Fig. 15 can now be recognized just below the center of the picture. Associated with the hair we have been following are three others, and this tendency for the hairs to group themselves in threes and fours is very noticeable. Some of the follicles are not so deeply seated as others and have their sebaceous glands in a plane higher up. This explains why no glands are to be seen in the vicinity of some of the follicles. The short, thick lines appearing here and there are arteries or veins wandering in and out of the plane of the section.

In Fig. 17 is shown the section forming the plane 0.30 millimeter below that of Fig. 15, or a total distance of 0.84 millimeter from the upper surface of the corneous layer. A cross section of the same hair as that shown in Figs. 14 and 15 appears in the center of the picture, but this time we have cut right through the hair bulb. The black mass is the bulb and the light patch at its center is the hair papilla. To the right and left and above the hair bulb are the sweat glands. They appear as large, empty sacs, with portions of their linings of epithelial cells showing like leopard spots. In this plane the elastin fibers are much less numerous than in the regions higher up and the collagen fibers are now much larger and grouped in bundles. At a distance of 0.12 millimeter below this plane, we encounter the last of the epithelial cells of the sweat glands and therefore the lower boundary of the thermostat layer.

The reticular layer consisted almost entirely of collagen fibers, elastin fibers being present only in the lowest region and surrounding the blood vessels and nerves traversing other parts of the reticular layer.

Calf Skin.

A calf skin, very naturally, appears much like a cow hide in miniature. In Fig. 18 is shown a vertical section from the skin of a healthy young heifer calf, which had been fixed in Erlicki's fluid immediately following the slaughter and flaying of the animal. As a rule, the skin of a heifer calf has greater solidity and fineness of appearance than that of a steer calf and is, consequently, to be preferred for leather making. In comparing Figs. 11 and 18, it should not be overlooked that the section of calf skin is magnified more than twice as highly as that of the cow hide. In fact, in making comparisons of any photomicrographs in the book, erroneous conclusions may be drawn, if the magnifications are not taken into consideration.

The relatively greater thickness of the thermostat layer in the calf

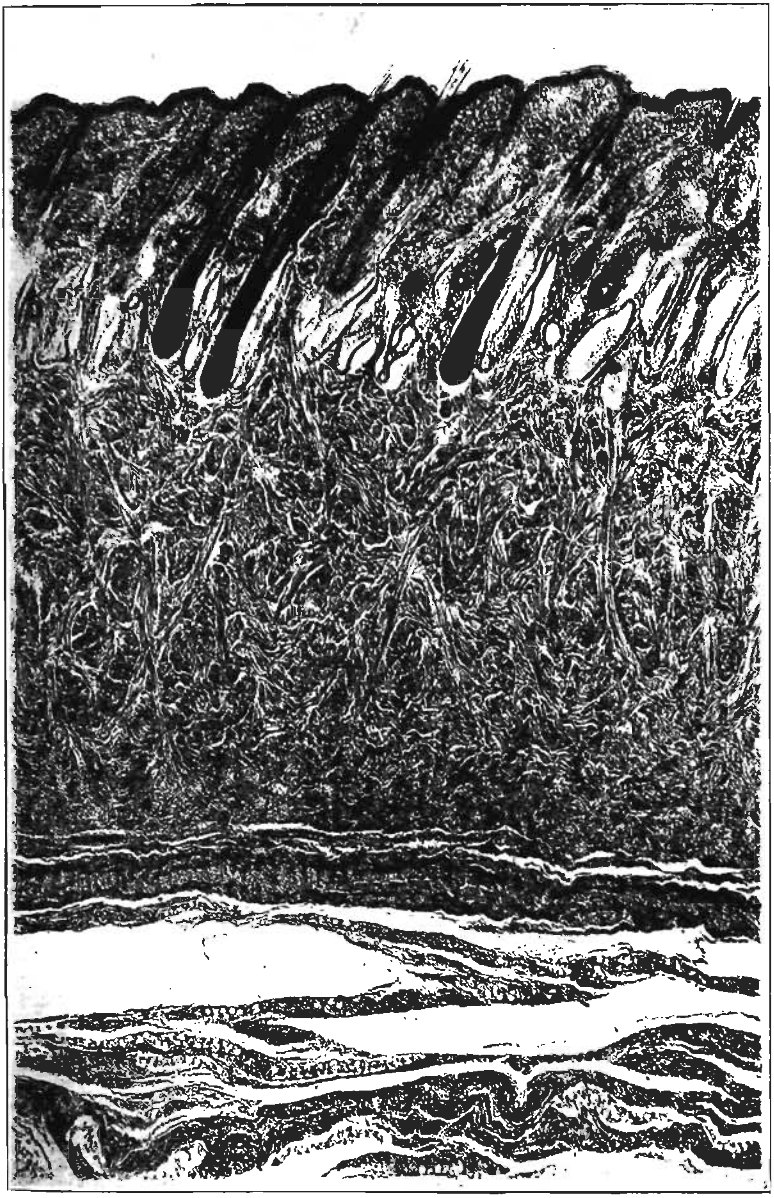


Fig. 18.—Vertical Section of Calf Skin.

Location: butt.
Thickness of section: 20 μ.
Stains: Van Heurck's logwood, Daub's bismarck brown.
Eyepiece: none.
Objective: 32-mm.
Wratten filter: F-red.
Magnification: 40 diameters.

skin is noticeable. This fact is doubly interesting because the structure of this layer is of much greater importance for calf skin than for cow hide; calf skins are generally used to make dressing and other leathers where fineness of appearance of the grain surface is highly valued, while cow hides more often are used for sole, belting, and harness leathers.

Another point to be noted in comparing Figs. 11 and 18 is that the sections were cut from exactly corresponding parts of the skins of the two animals. The importance of this point will be made clear from a study of Figs. 20 to 27. It is well known that a tanned skin is not uniform in structure throughout its entire area. The butt is usually much thicker and has greater solidity than any other part. The shanks are firm, but thin, while the flanks are thick, but spongy. In order to show how the structure of the skin varies in different regions, 8 strips were cut from the locations indicated in the diagram shown in Fig. 19. The skin was the same as that whose vertical section is shown in Fig. 18. Vertical sections of these 8 strips are shown in Figs. 20 to 27. In comparing the sections, it will be noted that the thickness of the thermostat layer is uniform throughout the skin, but that both the thickness and texture of the reticular layer vary widely.

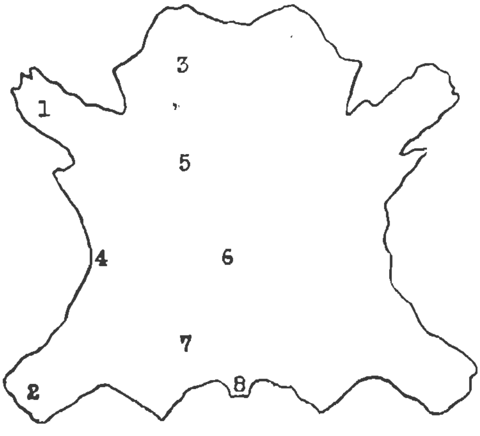


FIG. 19.—Diagram of Calf Skin showing locations of sections whose photomicrographs are shown in Figs. 20 to 27.

1: fore shank; 2: hind shank;
3: neck; 4: belly;
5: shoulder; 6: back bone;
7: butt; 8: tail.

The reticular layer is nearly 3 times as thick in the butt as in the hind shank. In the shoulder, the reticular layer is thinner than that of the butt and its fibers are somewhat finer. In the belly, the collagen fibers run nearly parallel to the grain surface and offer little resistance to any tendency to pull them apart in a vertical direction, whereas many of the fibers in the butt run nearly vertically, with some running in almost any direction, making this region very resistant to distortion. The grain surface appears less serrated on the butt than elsewhere. In fact, most of the differences observable in the various parts of finished leather may be attributed to initial differences in structure of the living skin.

In studying Fig. 18, use may be made of practically the entire description of cow hide given above. The bottom fifth of the picture shows the adipose tissue, consisting of rows of fat cells held together

by strands of connective tissues. The thick band forming the lower boundary of the derma is closely interwoven with elastin fibers, but between this region and the thermostat layer, as in the cow hide, there are very few elastin fibers.

A better view of the fibers of the reticular layer may be had by referring to Fig. 8, which shows some of the fibers appearing at the left hand side of Fig. 18, but at a much higher magnification.

Sheep Skin.

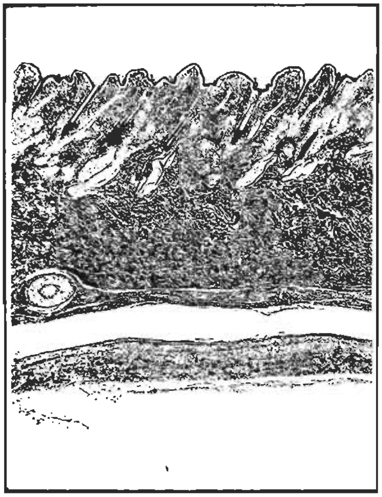
Fig. 28 shows a vertical section of the skin of a healthy sheep, fixed in Erlicki's fluid immediately after the death of the animal. Its structure is very different from that of the calf skin, both in the thermostat and reticular layers. A comparison of Figs. 18 and 28 indicates very plainly why sheep skin cannot be substituted for calf skin, where firmness and substance are desired. The collagen, or leather-forming, fibers of the sheep are extremely thin and not closely interwoven and tend to run parallel to the skin surface, which in itself makes for looseness of texture. Moreover, in the thermostat layer there are numerous sweat glands and fat cells, which leave empty spaces in the finished leather and make it very spongy.

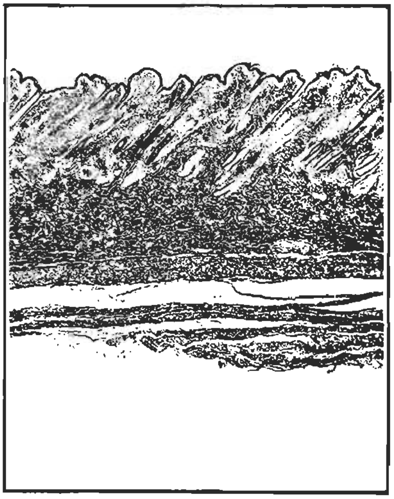
The proportion of fat cells to collagen fibers in sheep skins varies considerably according to the feeding of the animal, and there is often to be found an almost continuous layer of fat cells separating the two main layers of the skin. In such cases, it is desirable to separate the skin into its two layers before tanning and to tan each separately rather than to try to keep them together. Usually the skins are split into two parts after the liming process and the thermostat layers, called grains, are tanned with sumac or other tanning extract to make leather suitable for bookbinding, hat bands, etc., while the reticular layers are converted into chamois leather, for which they are particularly suitable, by means of a tannage with cod oil.

The dark, curved mass, very prominent in the upper, right hand of the picture and the smaller masses of similar appearance are portions of hair follicles. Unlike the follicles of the calf, those of the sheep turn and twist in every direction. We were unable to find one follicle lying wholly in a single plane. The curvature of these follicles is responsible for the curliness in the wool of the sheep. In the cow and calf, the hair is straight because the follicles are straight.

The twisting of the follicles makes the study of the structure of sheep skin more difficult than that of the calf. But the examination of several sections is sufficient to show that the general mechanism of the two skins is the same. Running from the top of the portion of hair follicle showing in the upper right part of the picture is a part of an erector pili muscle. The sebaceous glands appear to be very near the surface, while the sweat glands occupy much of the lower portion of the thermostat layer.

Sections from this skin at different stages of the tanning processes are shown in Chapters 8, 9, and 13 and should be examined in con-





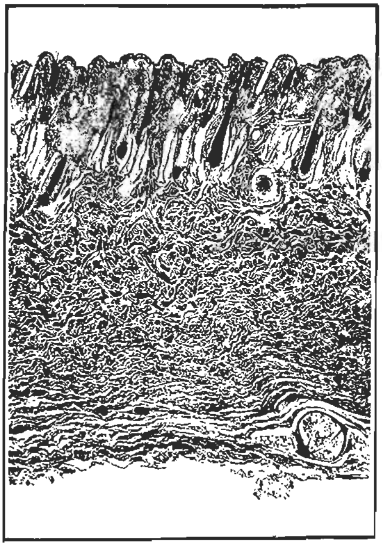


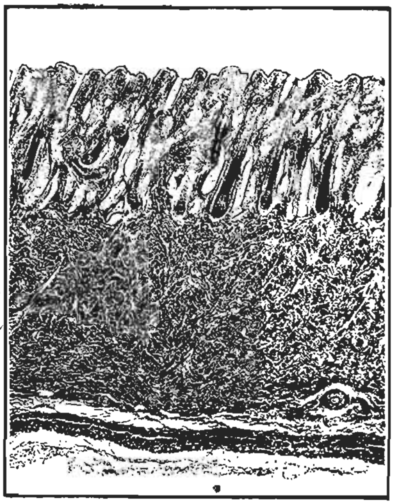
FIG. 20.—Fore Shank.
FIG. 22.—Neck.

FIG. 21.—Hind Shank.
FIG. 23.—Belly.

Vertical Sections of Calf Skin.

Locations: as noted.
Thickness of sections: 15 μ.
Stains: Van Heurck's logwood, Picro-indigo-carmine.

Eyepiece: none.
Objective: 32-mm.
Wratten filter: F-red.
Magnification: 15 diameters.



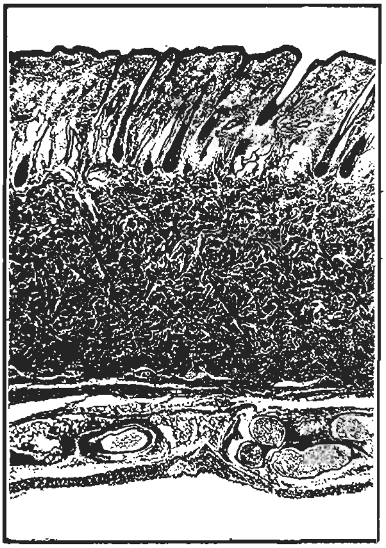


Fig. 24.—Shoulder.
Fig. 25.—Backbone.
Fig. 26.—Butt.
Fig. 27.—Tail.

Vertical Sections of Calf Skin.

Locations: as noted.
Thickness of sections: 15 μ.
Stains: Van Heurck's logwood, Picro-indigo-carmine.

Eyepiece: none.
Objective: 32-mm.
Wratten filter: F-red.
Magnification: 15 diameters.

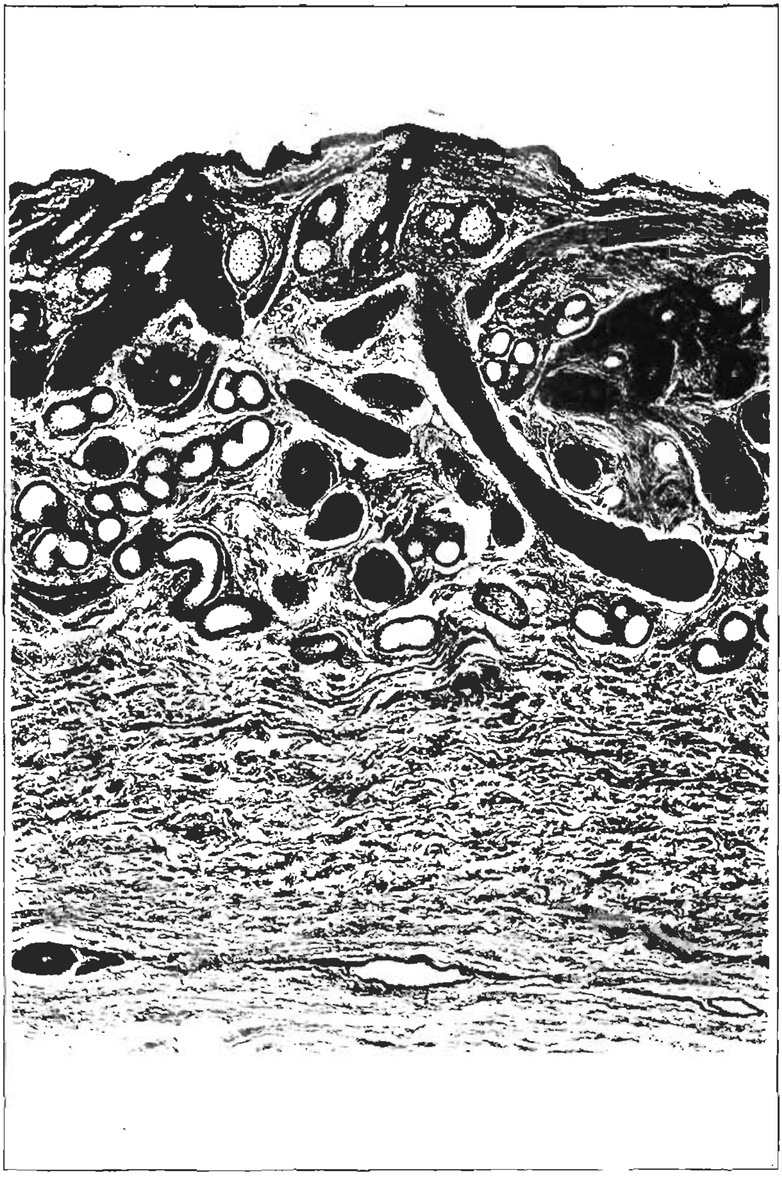


Fig. 28.—Vertical Section of Sheep Skin.

Location: butt.
Thickness of section: 20 μ.
Stains: Van Heurck's logwood, Daub's bismarck brown.

Eyepiece: none.
Objective: 16-mm.
Wratten filter: C-blue.
Magnification: 50 diameters.

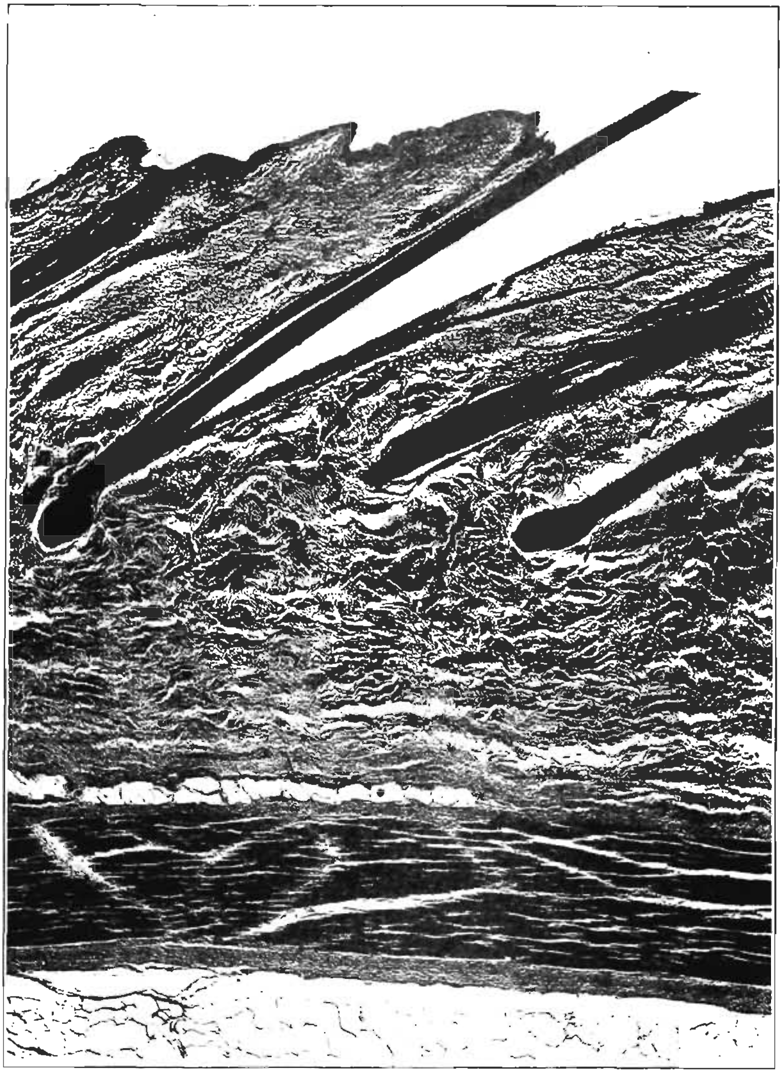


Fig. 29.—Vertical Section of Kid Skin.

Location: butt.
Thickness of section: 25 μ.
Stains: Van Heurck's logwood, Picro indigo-carmine.

Eyepiece: none.
Objective: 16 mm.
Wratten filter: H blue green.
Magnification: 50 diameters.

nection with the study of the raw skin. The epidermis can be differentiated more clearly by comparing Fig. 28 with Figs. 66 and 67 of Chapter 8. The general arrangement of the elastin fibers is best shown in Fig. 83 of Chapter 9.

The specimen of sheep skin shown was unusually free from the fat cells that tend to separate the skin into two layers. We were able to tan it into a reasonably firm piece of leather. A section of this leather is shown in Fig. 104 of Chapter 13. The leather was soft and somewhat spongy, but is probably a good example of the type of skin often substituted for kid skin in the manufacture of glove leather.

Goat Skin.

In many respects the skin of the goat may be regarded as having a structure intermediate between that of the calf and the sheep. The fibers are fuller and firmer than those of the sheep, but are hardly equal to those of the calf. The glands and fat cells, which are responsible for the sponginess of sheep leather, are very much less abundant in goat skin, although it must be admitted that this is largely dependent upon the animal's feeding. Both the goat and the sheep skins of the general market vary widely in quality and substance, a fact which warrants a considerable extension of the study of their structures. Calf skins, on the other hand, do not vary in quality nearly so widely.

Like the calf, the goat has straight follicles, and, consequently, straight hair. The surface of goat skin is very much coarser than that of calf skin. A glance at Fig. 9 will show that the pattern of the calf grain is considerably finer, even than that of the kid. Roughness of grain, however, is sometimes desirable and the grain surface of goat skins is often made still coarser by mechanical means.

A vertical section of kid skin is shown in Fig. 29. This was just an average domestic skin in the condition in which fresh skins are usually received at the tannery. The epidermis is the very thin dark line forming the upper boundary of the skin. It dips down into the derma, forming a nearly straight follicle, in which the hair grows. The erector pili muscle is the thin line running upward to the right from the base of the follicle. The opening of the sebaceous glands into the follicle can be seen just above the erector pili muscle. The fact that the collagen fibers run nearly parallel to the surface gives this skin, in its most solid part, a softness and looseness found only in the flanks of the calf skin.

Bounding the lower surface of the derma is a layer of striated muscle tissue, which permits the animal to twitch its skin. Muscles of this kind are often found on most of the various kinds of skins used for making leather.

A typical section of chrome tanned goat skin is shown in Fig. 146 of Chapter 14. It is interesting to compare its general structure with those of the calf and sheep.

Hog Skin.

The comparatively low value of hog skin for leather manufacture can be appreciated by studying the section shown in Fig. 30. The

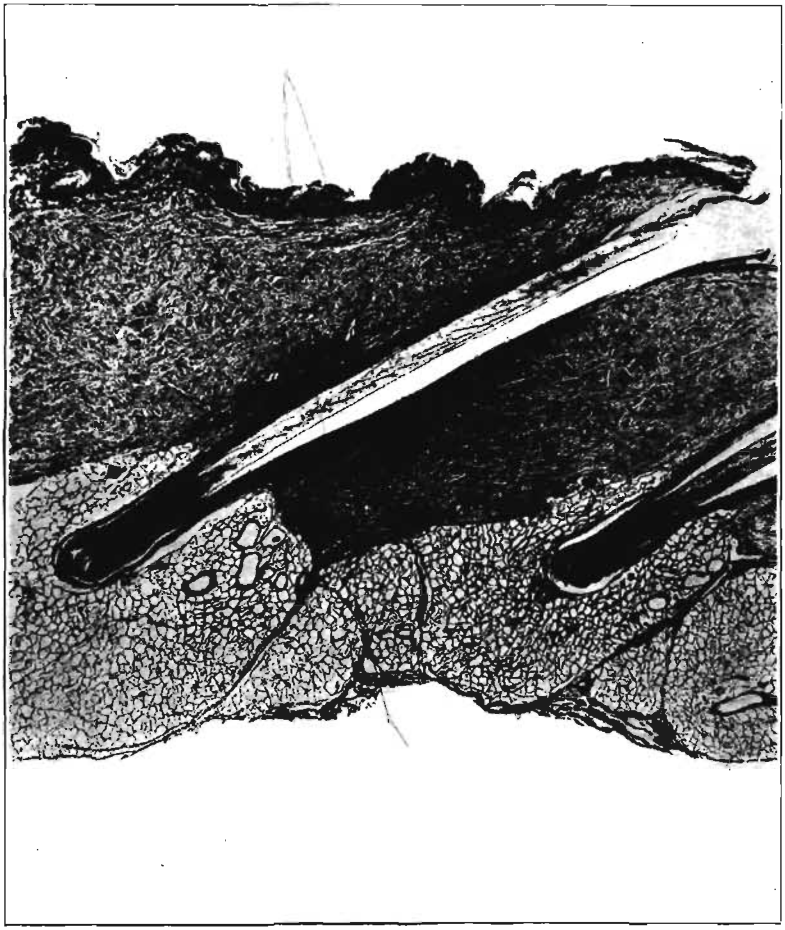


Fig. 30.—Vertical Section of Hog Skin.

Location: butt.
Thickness of section: 20 μ.
Stains: Friedlander's logwood, Daub's bismarck brown.
Eyepiece: none.
Objective: 48-mm.
Wratten filter: C-blue.
Magnification: 14 diameters.

reticular layer is composed chiefly of fat cells, which have practically no value in making leather. We have here a case where the general use of the term reticular is apt to be misleading. The fat cells extend

even up into the thermostat layer. The close relation of this structure to that of the human scalp, shown in Fig. 1, should be noted.

The epidermis, as well as the upper surface of the derma, is very rough and irregular in appearance. As in other skins, the epidermis dips down into the derma, forming the follicles in which the hairs, or rather bristles, grow. The hair bulbs are imbedded in the mass of fat cells which make up the reticular layer. These fat cells extend higher up into the thermostat layer in the region of each hair follicle, about which the fat cells form cone-shaped masses. The structure of a hair bulb from the hog is shown in Fig. 5.

The erector pili muscle belonging to the follicle shown in Fig. 30 did not lie in the plane of the section. A portion of one of these muscles can be seen in Fig. 84 of Chapter 9, which, because of its very much higher magnification, also shows the arrangement of the elastin fibers of the thermostat layer. The hog has relatively much fewer elastin fibers than the cow, calf, or sheep.

The roughness of the surface of the derma is further accentuated by the presence of papillæ, which seem to be rare in the skins of most of the lower animals studied. In the cow hide, papillæ were found only in the region of the legs, while in the calf, sheep, and goat skins, no papillæ were found at all. It would be interesting to determine whether the abundance of papillæ makes the hog more sensitive to touch and pain than the other lower animals. The extreme roughness of the grain surface of tanned hog skin is very noticeable in Fig. 9.

After the skin has been unhaired and prepared for tanning, only a portion of the thermostat layer remains. The follicles then are simply pockets lined with the grain membrane, the lower portions protruding out from the under side of the skin. When the tanned skin is shaved down on the under side to make it smooth, the bottoms of these pockets are cut away, leaving holes wherever there were bristles in the original skin. This serves further to lower the value of leather made from hog skin. A section of tanned hog skin is shown in Fig. 107 of Chapter 13.

Horse Hide.

The outstanding peculiarity of horse hide lies in the reticular layer. In the region of the butt there is a dense mass of collagen fibers in the reticular layer so compact as to render leather made from the butt naturally waterproof and nearly air tight. A section of horse hide taken from the butt is shown in Fig. 31. The dense mass of fibers, often called the glassy layer, can be seen running horizontally across the middle of the picture and appearing much darker than the remaining fibers. The portion of the hide containing the glassy layer is known as the shell and is used to make the leather sold under the name of cordovan. The rest of the hide not only does not have this glassy layer, but the fibers of the reticular layer are very loosely inter-

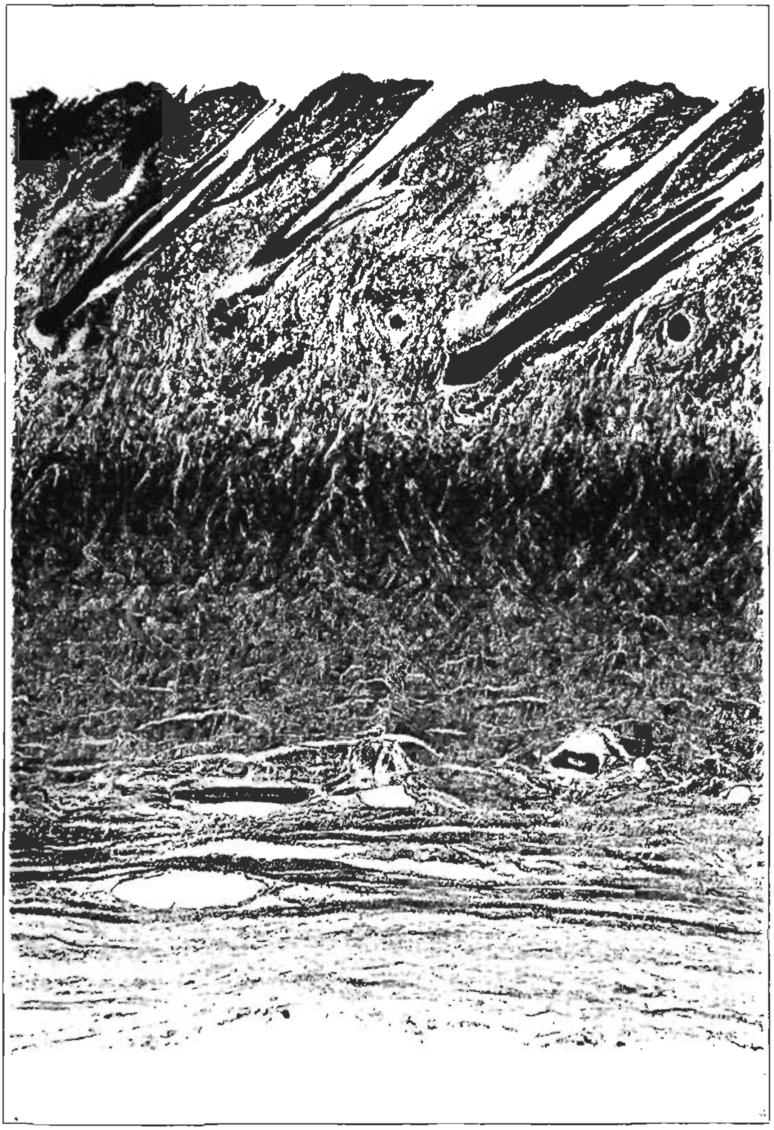


Fig. 31.—Vertical Section of Horse Hide.

Location: butt.
Thickness of section: 20 μ.
Stains: Van Heurck's logwood, Daub's bismarck brown.

Eyepiece: none.
Objective: 32-mm.
Wratten filter: C-blue.
Magnification: 25 diameters.

woven, giving the leather made from it a spongy substance that limits its use.

The thermostat layer of horse hide resembles that of cow hide. The general arrangement of the hair follicles, the erector pili muscles, and the sebaceous glands can be seen in Fig. 31, but the full detail shown in the sections of cow hide is lacking because the specimens of horse hide were not fixed immediately after the death of the animal, as in the case of the cow hide. The section, however, represents a hide in probably the usual condition in which horse hides are received at the tannery.

Figs. 105 and 106 of Chapter 13 show a comparison of leather made from the shell and that made from the portion of hide immediately adjoining the shell. In splitting the leathers to a nearly uniform thickness, the knife of the splitting machine cuts through the lower part of the glassy layer. The greatest contrast between the two specimens is thus shown in the lower portions.

Guinea Pig Skin.

A section of guinea pig skin is shown in Fig. 32 as an example of very small skins. Such skins can be made into fairly good leather, but their diminutive size limits the demand for them and it is questionable whether such leather could be sold at a profit. A point worthy of note is that the thermostat layer of the guinea pig skin is of practically the same thickness as that of a calf skin, which is very much larger. As shown in the description of the different parts of the calf skin, when nature provides a thinner skin, she does so almost entirely at the expense of the reticular layer, and not of the thermostat layer. It is possible that a minimum thickness for any size of animal is required for the proper operation of this important layer.

The corneous layer of the epidermis appears like a few strands of delicate threads just above the Malpighian layer, the dark line bounding the upper side of the derma. The collagen fibers of the reticular layer are so fine that they appear only as thin threads even at a magnification of 70 diameters. The dark band crossing the bottom of the picture is a mass of striated muscle tissue.

Fish Skins.

The detailed structure of fish skins is very different from those of mammals. Nevertheless fish skins yield a leather comparing favorably with some of the more common types of commercial leathers. Fish leather is very tough, as a rule, and is suitable for many purposes where great strength is required. Sturgeon leather used for lacing heavy belts together has been known to outwear the belts. It is said that the people of New England, in the old days, made shoes and gloves from the skin of the cod fish. Other fish skins are sometimes used for making fancy leathers.

In Figs. 33, 34, and 35 are photomicrographs of sections of the

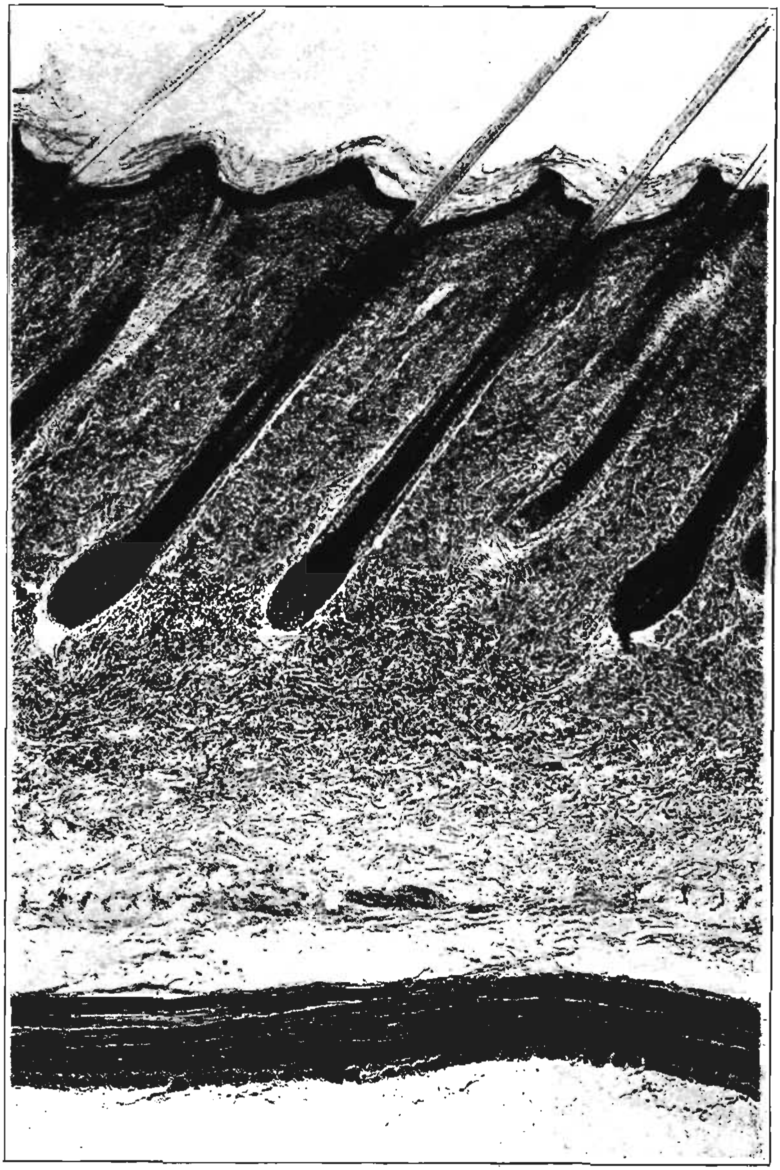


Fig. 32.—Vertical Section of Guinea Pig Skin.

Location: butt.
Thickness of section: 30 μ.
Stains: Van Heurck's logwood, Picro-indigo-carmine.

Eyepiece: none.
Objective: 16-mm.
Wratten filter: F-red.
Magnification: 70 diameters.

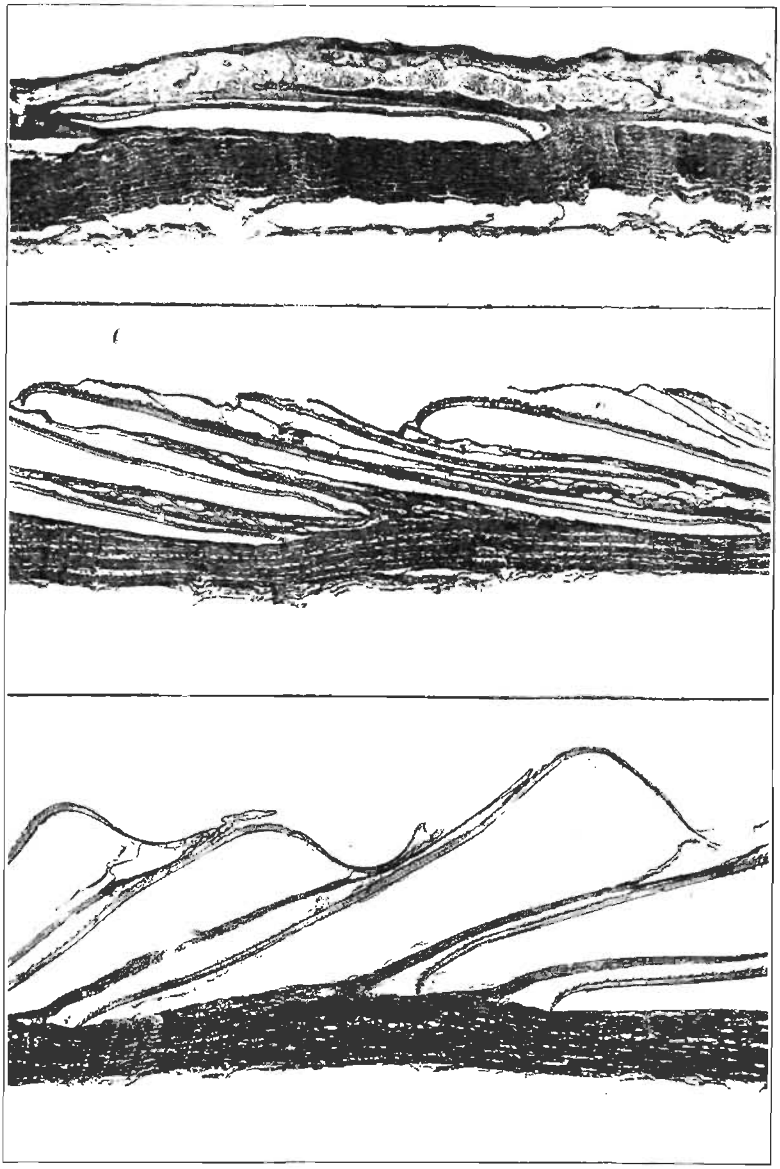


Fig. 33.—Vertical Section of Halibut Skin.

Fig. 34.—Vertical Section of Cod Fish Skin.

Fig. 35.—Vertical Section of Salmon Skin.

Location: side.
Thickness of sections: 20 μ.
Stains: Friedlander's logwood, Picro-indigo-carmine.

Eyepiece: none.
Objective: 32-mm.
Wratten filter: H-blue green.
Magnification: 17 diameters.

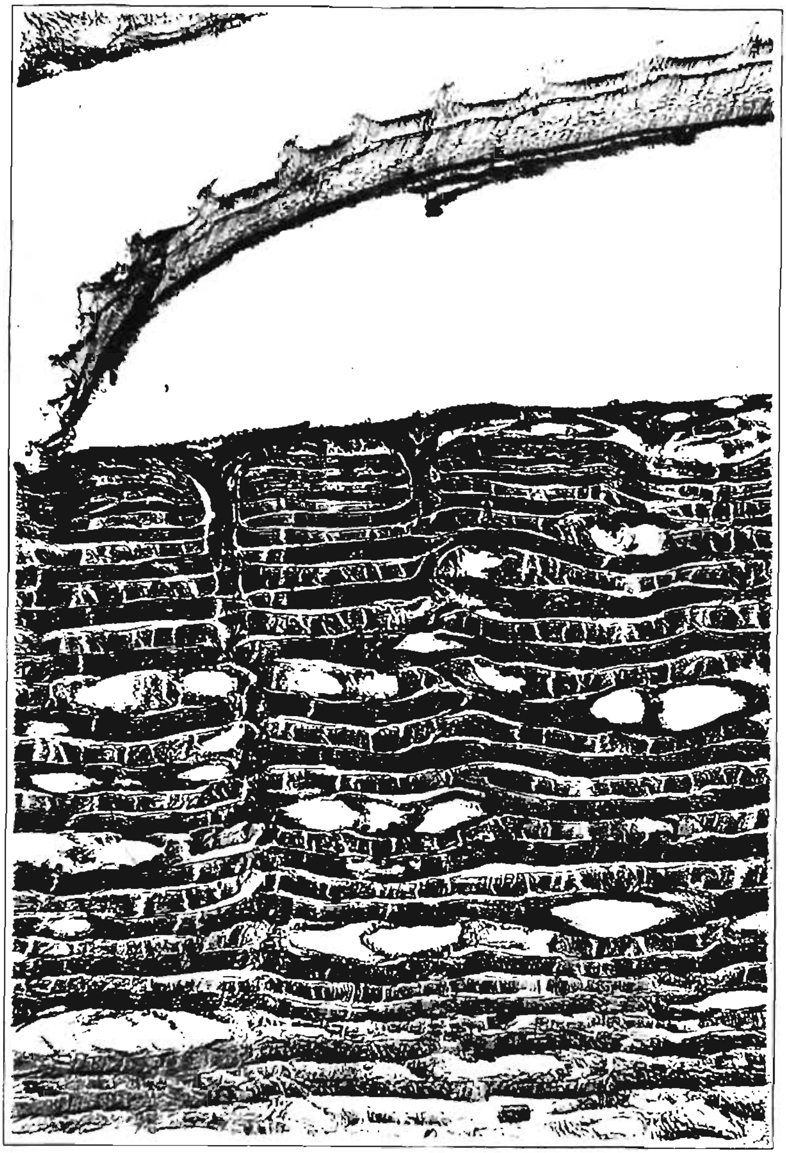


Fig. 36.—Vertical Section of Salmon Skin.

Location: side.
Thickness of section: 20 μ.
Stains: Friedlander's logwood, Picro-indigo-carmine.

Eyepiece: 7.5X.
Objective: 16-mm.
Wratten filter: H-blue green.
Magnification: 185 diameters.

skins of the halibut, cod, and salmon. These skins have a thin epidermis covering them and which dips into the derma here and there forming follicles in which the scales grow. The scales of the fish correspond to the hairs of the warm blooded animals. The scales may be recognized by their saw-tooth edges.

A portion of the right hand side of Fig. 35 is shown in Fig. 36 at a very much higher magnification so as to show the detailed structure of the derma. The upper portion of the picture is occupied by the lower end of a scale. We have not yet identified in fish skin the machinery of a thermostat layer like that common to the skins of mammals and, being cold blooded, they probably have none. Instead of interlacing bundles of collagen fibers, ribbons of collagen running parallel to the surface make up the major portion of the skin. These ribbons do not interlace, but here and there we note bands of collagen running vertically through the skin. This adds greatly to the strength of the skin and prevents the distortion made possible in a vertical direction where all the fibers or ribbons run horizontally.

A section of tanned salmon skin, with the epidermal system completely removed, is shown in Fig. 108 of Chapter 13. This leather is purposely shown in the unfinished state because the structure is thus shown more clearly. In finishing such leather, either the loose, upper portion is rolled out smoothly and coated with a finishing material or it is shaved off and the under portion is treated with a suitable finish and embossed or plated.

Other Skins.

The descriptions of skin structure given above are the result of an investigation still in progress and far from complete. But it appears that what has thus far been accomplished represents a real advance and that it is desirable to present as much as possible of what has been learned to date, even though the subject is incomplete. In the chapters on tanning, sections of leather appear which were made from skins of which we have not yet made a study. These may profitably be consulted in connection with the study of histology.

In Fig. 110 is shown a section of alligator leather. The structure of the fibers, or ribbons, in many ways resemble those of the fishes. A somewhat similar structure may be noted in the section of shark leather in Fig. 109. The uninviting hooks on the surface of the shark leather are hardly visible to the naked eye and give the leather a harsh feel. There are, of course, many kinds of sharks and it is not customary to leave these hooks on the leathers placed on the market. The fibrous structure of the horned-toad leather shown in Fig. 111 also resembles that of the fishes. In contrast to the smaller skins is the section of hippopotamus leather shown in Figs. 115 and 116. Other interesting types of leather are those of the camel and walrus, shown in Figs. 112, 113, and 114.

Chapter 3.

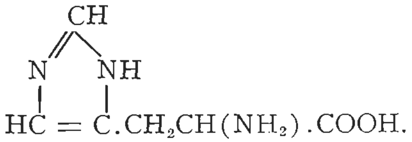
Chemical Constituents of Skin.

By far the greater portion of the solid matter of the skin consists of protein matter. The proteins form one of the most important and complex groups of organic compounds and are remarkable for the number of general physical and chemical properties which they possess in common and the extreme difficulty of making quantitative separations of the several members of any one group. They all contain carbon, hydrogen, nitrogen, and oxygen, and many of them also contain sulfur and phosphorus. They are all amphoteric, combining with both acids and bases, and those that do not dissolve in water swell by absorbing water. They are more or less readily hydrolyzed by boiling acid or alkaline solutions or by appropriate solutions of enzymes. Hydrolysis proceeds in steps yielding in turn bodies of decreasing complexity, the proteoses, peptones, polypeptides, and finally simple amino acids. Amines and ammonia are often found among the various hydrolytic products. The following amino acids have been isolated and identified from the hydrolytic products of different proteins: [1]

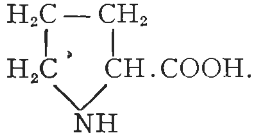
1. Glycine, *aminoacetic acid,* $NH_2.CH_2.COOH$.
2. Alanine, *α-aminopropionic acid,* $CH_3.CH(NH_2).COOH$.
3. Valine, *α-aminoisovalerianic acid,* $(CH_3)_2:CH.CH(NH_2).COOH$.
4. Leucine, *α-aminoisocaproic acid* $(CH_3)_2:CH.CH_2.CH(NH_2).COOH$.
5. Isoleucine, *α-amino-β-methyl-β-ethylpropionic acid,* $(CH_3.CH.C_2H_5).CH(NH_2).COOH$.
6. Phenylalanine, *β-phenyl-α-aminopropionic acid,* $C_6H_5.CH_2.CH(NH_2).COOH$.
7. Tyrosine, *β-parahydroxyphenyl-α-aminopropionic acid,* $HO.C_6H_4.CH_2.CH(NH_2).COOH$.
8. Serine, *β-hydroxy-α-aminopropionic acid,* $CH_2(OH).CH(NH_2).COOH$.
9. Cystine, *di-(β-thio-α-aminopropionic acid),* $HOOC.CH(NH_2).CH_2.S\text{-}S.CH_2.CH(NH_2).COOH$.
10. Aspartic acid, *aminosuccinic acid,* $HOOC.CH_2.CH(NH_2).COOH$.

[1] Cf. Chemical Constitution of the Proteins. R. H. A. Plimmer. Longmans, Green & Co., London.

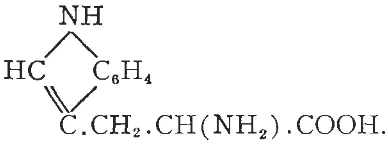
11. Glutamic acid, *α-aminoglutaric acid*, $HOOC.CH_2.CH_2.CH(NH_2).COOH$.
12. Arginine, *α-amino-δ-guanidinevalerianic acid*, $HN:(C.NH_2).NH.CH_2.CH_2.CH_2.CH(NH_2).COOH$.
13. Lysine, *α-ε-diaminocaproic acid*, $NH_2.CH_2.CH_2.CH_2.CH_2.CH(NH_2).COOH$.
14. Caseinic acid, *diaminotrioxydodecanic acid*, $C_{12}H_{26}N_2O_5$.
15. Histidine, *β-iminazolyl-α-aminopropionic acid*,



16. Proline, *α-pyrrolidinecarboxylic acid*,



17. Oxyproline, *oxypyrrolidinecarboxylic acid*, $C_5H_9NO_3$.
18. Tryptophane, *β-indole-α-aminopropionic acid*,



Under suitable conditions, amino acids can be made to combine with each other by removing the elements of water, the amino group of one combining with the carboxyl group of another, thus

$$CH_3.CH(NH_2).COOH + NH_2.CH_2.COOH = CH_3.CH(NH_2).CO.NH.CH_2.COOH + H_2O.$$

A combination of two amino acids is called a dipeptide, one of three a tripeptide, etc. Fischer[2] succeeded in preparing the octadecapeptide

$$NH_2 . CH(C_4H_9) . CO . [NHCH_2CO]_3 . NH . CH(C_4H_9) . CO. [NHCH_2CO]_3.NH.CH(C_4H_9).CO.[NHCH_2CO]_8.NH . CH_2.COOH,$$

which contains 15 glycine and 3 leucine residues and has a molecular weight of 1213. It gives the biuret test for protein, is precipitated from solution by tannin, and would have been classed as a protein had it been found in nature. Later Abderhalden and Fodor[3] succeeded in

[2] Synthesis of Polypeptides. Emil Fischer. *Pr. Chem. Soc.* 23, 82; *C. A.* 1 (1907), 1545.
[3] Synthesis of Polypeptides of High Molecular Weight from Glycocoll and l-Leucine. E. Abderhalden and A. Fodor. *Ber.* 49 (1916), 561; *C. A.* 10 (1916), 1531.

preparing a polypeptide containing 15 glycine and 4 leucine residues and having a molecular weight of 1326.

The close resemblance of the more complex polypeptides to the natural proteins and to their first products of decomposition, the proteoses and peptones, and the fact that all proteins yield amino acids upon complete hydrolysis have established the view that the general structure of proteins is at least similar to that of the polypeptides. The above list of amino acids indicates the tremendous number of possible combinations to form proteins and of the isomeric forms that any individual protein may have.

The generally accepted methods of classifying proteins are based upon differences in solubility, speed of hydrolysis, and precipitability under definite conditions. But, since a small amount of foreign matter may alter these properties entirely for a given protein and because of the difficulty of separating and purifying proteins, this system of classification is not wholly satisfactory, although it is, perhaps, the best available at the present time. The common names applied to proteins, such as keratin, albumin, etc., do not represent individual substances, but groups of closely related proteins whose quantitative separation is very difficult.

The most important classes of skin proteins, in the order of increasing importance to the tanner, are the mucins, albumins, globulins, melanins, keratins, elastins, the unnamed proteins of the grain surface, and the collagens. Except in the case of fur skins, the first five classes are of importance only because they must be removed from the skin prior to tanning, without injuring the remaining protein matter. In general, the albumins are the only skin proteins soluble in pure water. The globulins are soluble in dilute salt solutions and the mucins and melanins in dilute alkalies. The four remaining classes, which belong to the general group of proteins known as albuminoids, are insoluble in dilute solutions of acids, bases, or salts at room temperature, but all are dissolved and hydrolyzed by boiling solutions of concentrated acids or alkalies. The keratins are dissolved by strongly alkaline solutions before the remaining three classes are seriously attacked and the elastins are easily dissolved by trypsin before any injury is done to the collagen or grain surface. In boiling water, the collagen goes into solution as gelatin, leaving behind a residue of elastin and the proteins of the grain surface.

The albumins and globulins are found in the blood and lymph of the skin and also in the fluids of the muscles and nerves. By extracting powdered dog skin with a 10-per cent solution of sodium chloride, under toluene at 37° C., Rosenthal [4] obtained a quantity of albumins and globulins which, upon coagulating, washing with water, alcohol, and ether, and drying, gave a weight equal to 24 per cent of the total protein of the skin. But a yield of only 4.2 per cent was obtained from calf skin.

The albumins are soluble in pure water or in dilute solutions of

[4] Biochemical Studies of Skin. G. J. Rosenthal. *J. Am. Leather Chem. Assoc.* 11 (1916), 463.

acids, bases, and salts, but are precipitated by the addition of concentrated mineral acid or by saturating a weakly acid solution with salt. Their solutions coagulate upon boiling, in the presence of a small amount of salt.

The globulins generally are insoluble in pure water at the neutral point, but dissolve in dilute neutral salt solutions, from which they can be precipitated by sufficient dilution or by saturating the solution with salt, being most readily soluble in salt solutions of moderate concentration. They dissolve freely in dilute solutions of acids and alkalies. Like albumins, their solutions coagulate upon heating. Fibrinogen, an important constituent of the blood, is usually classed as a globulin, but differs from serum globulin in being precipitated from solution by a lesser concentration of neutral salt and of coagulating at a lower temperature. It tends to clot upon exposure to air, forming the insoluble protein fibrin, which action is favored by rise of temperature or agitation and is hindered by cooling or the addition of acids, alkalies, or concentrated salt solutions. The clotting action is supposed to be due to the action of an enzyme, thrombin, which is not a normal constituent of blood, but which is formed from the leucocytes and blood plates in the presence of calcium salts.

The mucins are conjugated proteins, of the group known as glycoproteins, containing both protein and carbohydrate groups in their molecules. They are insoluble in pure water, but, in faintly alkaline solution, give mucilaginous solutions which are precipitated by the addition of acid. It is questionable whether mucins are abundant in the skins of mammals. It has often been assumed that the mucins form the elusive "interfibrillary cementing substance" of the skin, but the existence of a cementing substance in the fibers, other than collagen itself, has not been clearly demonstrated.

Rosenthal [5] extracted calf skin, previously freed from albumins and globulins, with half-saturated lime water under toluene. Upon rendering the extract acid with hydrochloric, protein matter was precipitated, which was washed with dilute acid, water, alcohol, and ether, and dried and weighed. The yield of protein, which he called mucoid, equalled about 2.7 per cent of the total protein matter of the skin. The yield from the solid part of the butt was 4.8 per cent against only 1.2 per cent for the loose portions of the belly. Although mucoids are dissolved by dilute alkalies and precipitated by rendering the solution acid, doubt is thrown on Rosenthal's interpretation of his results by the experiments of Thompson and Atkin,[6] who showed that hair and wool are partly dissolved by lime liquors and that some of the matter dissolved is precipitated by rendering the solution slightly acid. Since the newly formed epithelial cells are very much more easily attacked than hair and wool, much of the material isolated by Rosenthal may actually have been derived from this source.

No very sharp line of distinction can be drawn between the mucins

[5] *Loc. cit.*

[6] Note on the Analysis of Lime Liquors. F. C. Thompson and W. R. Atkin. *J. Soc. Leather Trades' Chem.* 4 (1920), 15.

and the mucoids. Hammarsten [7] differentiates between them as follows: "The *true mucins* are characterized by the fact that their natural solutions, or solutions prepared by the aid of a trace of alkali, are mucilaginous, ropy, and give a precipitate with acetic acid which is insoluble in excess of acid or soluble only with great difficulty. The *mucoids* do not show these physical properties, and have other solubilities and precipitation properties."

The melanins are proteins of intense color, usually reddish-brown to black, constituting the pigment of the hair and epithelial cells. They are insoluble in water and dilute acids, as a rule, but dissolve more or less readily in dilute alkalies. They may be extracted with boiling dilute alkali and precipitated by the addition of acid. They contain variable amounts of iron and sulfur in combination.

The origin of the melanins is not known with certainty, although it seems probable that they are derived from the blood and lymph. Their development is accelerated by frequent exposure to strong sunlight. Prolonged exposure is followed by a rush of blood to the skin and the production of pigment to protect the tissues against the action of the intense light. This shows itself in the apparent darkening of the color of the skin. The coloring matter of the blood, hemoglobin, belongs to the class of conjugated proteins known as chromoproteins and, like the melanins, also contains iron and sulfur.

That the blood and lymph contain substances capable of reacting to produce deeply colored bodies is well appreciated by the tanners. Skins from which the blood and lymph have not been washed are liable to develop stains very difficult to remove, unless special precautions are taken, which will be discussed in Chapter 6 in connection with the preservation of skin to be kept for a considerable period before tanning.

The chief constituent of the epidermal system, including the epidermis, hair, and epithelial cells of the glands, is the class of proteins known as keratin. The general method of preparing this material for examination is to boil the finely divided sample containing it with water and then to digest the residue with an acid pepsin solution followed by an alkaline trypsin solution and then to wash it thoroughly with water, alcohol, and finally with ether.

Keratin differs chemically from other classes of proteins in yielding a comparatively large amount of cystine, upon hydrolysis. In the following table are given the yields of amino acids obtained from keratins from different sources along with those from samples of elastin and collagen, or gelatin. The differences shown by keratins from different sources is interesting, but each sample analyzed probably consisted of a mixture of different keratins more or less contaminated by other proteins.

Keratin prepared in the manner described above is naturally very resistant to the action of dilute acids and alkalies, pepsin, trypsin, and boiling water, but it is dissolved by strong alkalies and by water heated

[7] Physiological Chemistry. O. Hammarsten. Translation by J. A. Mandel. John Wiley & Sons, New York.

TABLE I.

Amino Acid	Horse Hair [8]	Keratin from Sheep Wool [9]	Keratin from Sheep Horn [9]	Goose Feathers [10]	Elastin [11]	Collagen or Gelatin [12]
	Per Cent Amino Acid Obtained from					
Glycine	4.7	0.6	0.5	2.6	25.8	25.5
Alanine	1.5	4.4	1.6	1.8	6.6	8.7
Valine	0.9	2.8	4.5	0.5	1.0	0.0
Leucine	7.1	11.5	15.3	8.0	21.1	7.1
Serine	0.6	0.1	1.1	0.4	...	0.4
Aspartic acid	0.3	2.3	2.5	1.1	...	3.4
Glutamic acid	3.7	12.9	17.2	2.3	0.8	5.8
Cystine	8.0	7.3	7.5	...	...	...
Phenylalanine	0.0	...	1.9	0.0	3.9	1.4
Tyrosine	3.2	2.9	3.6	3.6	0.3	0.01
Proline	3.4	4.4	3.7	3.5	1.7	9.5
Oxyproline	...	...	...	...	...	14.1
Histidine	0.6	...	...	...	...	0.9
Arginine	4.5	...	2.7	...	0.3	8.2
Lysine	1.1	...	0.2	...	...	5.9

to 150° C. under pressure. The method of preparation may be criticized on the ground that it does not include young keratin. On the other hand, it may be contended that the proteins of newly formed epithelial cells are not keratins at first, but are later converted into keratins. However, the changes in properties with age are so gradual as to make it almost impossible to draw any sharp line of demarcation. This is a good example of the difficulty of trying to classify proteins strictly according to properties. The cells of the Malpighian layer of the epidermis are readily attacked by trypsin and by solutions of ammonia, but become very much more resistant as they are pushed upward into the corneous layer.

In the *stratum granulosum* of the epidermis, the protoplasm of the epithelial cells has dried up and appears like granules inside of the cells. Walker [13] regards these granules as consisting of two substances, keratohyalin and eleidin, presumably stages in the transformation of the protoplasm into the wax and fatty material with which the cells of the corneous layer of the epidermis are loaded.

The yellow, elastic fibers interlacing the outer layers of the derma and enveloping the nerves and blood vessels are made up of a class of proteins called elastin. The tendons of the body have been the chief source of elastin used for study, in particular the *ligamentum nuchæ*, the tendon at the back of the head of the ox. F. L. Seymour-Jones [14] found that a piece of *ligamentum nuchæ* of about 1 square centimeter cross section gave on a testing machine an extension of 150 per cent before breaking, the strain being too small to measure; less than 5 lbs.

[8] Abderhalden and Wells. *Z. physiol. Chem.* 46 (1905), 31.
[9] Abderhalden and Voitinovici. *Ibid.*, 52 (1907), 348.
[10] Abderhalden and Le Count. *Ibid.*, 48 (1905), 40.
[11] Abderhalden. Lehrbuch der physiol. Chem. (1909).
[12] H. D. Dakin. *J. Biol. Chem.* 44 (1920), 524.
[13] Dermatology. N. Walker. Wm. Wood & Co., New York.
[14] Chemical Constituents of Skin. F. L. Seymour-Jones. *J. Ind. Eng. Chem.* 14 (1922), 130.

He also found that the tendon was slowly digested by lime water, although the action may have been due to bacteria.

Elastin may be prepared for study by extracting this tendon with dilute sodium chloride solution, washing and then boiling it with water, then with a 1-per cent solution of potassium hydroxide, again with water, and then with acetic acid. The residue is then treated with cold 5-per cent solution of hydrochloric acid for 24 hours, thoroughly washed with water, boiled again with water, and then washed with alcohol and ether and dried. It then has a yellowish-white appearance. It is not dissolved by boiling water nor by acids and alkalies in the cold, but is easily dissolved by concentrated mineral acids upon heating. The yields of the different amino acids from a sample of elastin are given in Table I.

It is, of course, not safe to assume that elastin from skin has exactly the same properties as that from other parts of the body, but the difficulty of isolating some of the skin proteins for study has made it desirable to investigate proteins of the same general classes from parts of the body where they are more easily available, if only to get a suggestion of the properties of the skin proteins. Actually we do find that the elastin of skin behaves much like that from the *ligamentum nuchæ,* being resistant to boiling water and to cold solutions of acids and alkalies. In glue manufacture, much of the elastin remains in the scutch or residue left after boiling the skin in water. By examining sections of skin under the microscope, after special treatments, we have found that the elastin fibers are not appreciably attacked by dilute solutions of acids and alkalies or by tannery lime liquors, but are easily dissolved by neutral trypsin solutions. These fibers apparently act so as to resist an increase in area of the grain surface of the skin.

The proteins of the grain surface are remarkably resistant to most of the ordinary chemical reagents. The thin fibers of this surface are not dissolved by solutions of caustic alkalies sufficiently strong to destroy the collagen fibers, epidermis and hair. In boiling water, they evidently undergo some change in composition, but remain undissolved in the form of a thin sheet while the collagen passes into solution as gelatin. They are apparently unaffected by trypsin solutions strong enough to dissolve all of the elastin fibers beneath them. But in contact with water having a pH value of about 6, they are easily attacked and liquefied by putrefactive bacteria, although this action can be checked by the addition of a sufficient amount of acid, alkali, or salt.

These fibers represent only a very small proportion of the skin by weight, but they are of great importance because they form the grain surface of finished leather, giving it its characteristic appearance. Their position in the grain surface is shown in Fig. 150 of Chapter 16. In tanning and dyeing, they take a color different from that assumed by the collagen fibers, which is noticeable when leather is cut. Any damage to the grain surface reduces the selling value of the leather materially.

Collagen is the most abundant protein of the skin and the one of greatest importance to the tanner, since it is the basis of leather. It constitutes the bulk of the substance of the white fibers of the connective tissues of the derma.

Collagen can be prepared for study from fresh skin by removing the other constituents. The adipose tissue is carefully cut away and the skin thoroughly washed. It is then extracted with several changes of 10-per cent sodium chloride solution, in a closed jar set in a tumbling machine, or agitator, in order to remove the soluble protein matter. It is then put back into the same jar with a one-tenth-per cent solution of sodium sulfide containing lime well in excess of saturation and tumbled occasionally for several days, or until the hair is quite loose.

The hair and epidermal matters are then removed by scraping the grain surface with a knife blade. The entire grain surface is then cut away, preferably on a splitting machine. The skin is then washed thoroughly to remove most of the lime and is then digested for 5 hours at 40° C. with a solution containing 1 gram of U. S. P. pancreatin, 2.8 grams of monosodium phosphate, and 18 cubic centimeters of molar sodium hydroxide per liter. This removes all of the elastin fibers. The skin is then cut into small pieces and put into a jar of water equipped with a stirring device. Hydrochloric acid is added at such rate as to maintain the solution just faintly acid to methyl orange. When no more acid is required, the pieces are left to wash in running tap water over night. Next day they are soaked in several changes of alcohol to remove the water and then in xylene, after which they are exposed to air until the xylene has evaporated. They are then ground in a mill to a fibrous powder. Collagen thus prepared is known as hide powder.

Upon heating with water to 70° C., collagen slowly passes into solution as gelatin. But just what relation gelatin bears to its parent substance collagen is not known with certainty. Hofmeister[15] suggested that collagen is an anhydride of gelatin and that the change from one to the other is reversible, collagen being regenerated by drying gelatin at 130° C. This heating changes the properties of gelatin so that it swells in water to a lesser extent than before and passes into solution with greater difficulty. In commenting upon Hofmeister's work, Alexander[16] says "It is extremely doubtful if collagen is regenerated under these conditions, the more probable explanation being that, upon driving off the water, the constituent particles of the gelatin approach so close as to form an irreversible gel, thus rendering it insoluble."

C. R. Smith[17] found that gelatin dried at 100° C. and then heated to 128° loses 1.25 per cent in weight. It then swells very slowly and dissolves in water at 35° to 40°, with nearly complete restoration of its jellying power. He concedes that gelatin dried at 128° may

[15] *Z. physiol. Chem.* 2 (1878), 299.
[16] Allen's Commercial Organic Analysis. Vol. 8 (1913), p. 586.
[17] Mutarotation of Gelatin and Its Significance in Gelation. C. R. Smith, *J. Am. Chem. Soc.* 41 (1919), 135.

be converted into collagen, but that collagen itself may represent a form of gelatin which is difficult to disperse. Emmett and Gies,[18] on the other hand, suggest that the conversion of collagen into gelatin involves an intramolecular rearrangement.

Plimmer[19] says "those proteins which are resistant to the action of trypsin until they have been acted upon by pepsin will have all their units contained in the anhydride ring." Gelatin is easily hydrolyzed by either pepsin or trypsin, while it has been generally believed that collagen is hydrolyzed by pepsin, but not by trypsin. This led the author[20] to suggest that Plimmer's statement corroborated Hofmeister's view of the anhydride structure of collagen. But Thomas and Seymour-Jones[21] have recently demonstrated that collagen is attacked by trypsin under the right conditions. The erroneous view that collagen is resistant to tryptic digestion unless previously swollen with acid or alkali dates back to a series of studies by Kühne,[22] Ewald and Kühne,[23] and Ewald,[24] which were based only upon qualitative observations.

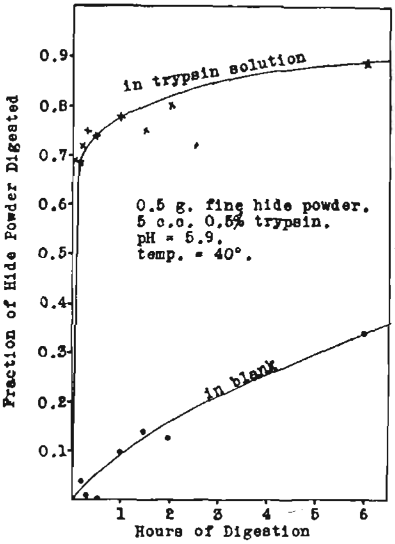


FIG. 37.—Rate of digestion of hide powder by trypsin as a function of time.

Thomas and Seymour-Jones found that trypsin acts most rapidly upon collagen at a pH value of 5.9 and that the action is not appreciably accelerated by soaking the protein previously in solutions of higher or lower pH values such that the protein is not actually hydrolyzed by the acid or alkali. In studying the effects of time and concentration of enzyme upon the digestion of hide powder by trypsin, they adopted the following precedure. In each experiment 0.5 gram of hide powder was placed in a centrifuge tube having a capacity of 10 cubic centimeters and a conical bottom graduated in units of 0.1 cubic centimeter. In order to bring the hide powder to the optimum pH value, they covered it with 5 cubic centimeters of a phosphate buffer solution having a pH value of 5.9 and a few drops of toluene to check bacterial action. The tube was shaken for 3 hours, then centrifuged for 20 minutes at 1000 times gravity, and the volume of hide powder read from the

[18] *J. Biol. Chem.* 3 (1907), 33.
[19] *Loc. cit.*
[20] Theories of Leather Chemistry. J. A. Wilson. *J. Am. Leather Chem. Assoc.* 12 (1917), 108.
[21] Hydrolysis of Collagen by Trypsin. A. W. Thomas and F. L. Seymour-Jones. *J. Am. Chem. Soc.* (1923); Dissertation, F. L. Seymour-Jones. Columbia University, 1923.
[22] W. Kühne. *Verhande. Naturhist. Med. Ver.*, Heidelberg, 1 (1887), 198.
[23] A. Ewald and W. Kühne. *Ibid.*, 1 (1887), 451.
[24] A. Ewald. *Z. Biol.* 26 (1890), 1.

graduations in the tube. The supernatant liquor was then run away and replaced by 5 cubic centimeters of trypsin solution having a pH value of 5.9 or by the buffer solution where a blank was being run. Toluene was added in every case as a safeguard. The solution was shaken in a thermostat at 40° C. for a stated length of time and then centrifuged and the volume of hide powder again read, the loss in volume being taken as a measure of the amount of hide powder dissolved.

The rate of digestion of hide powder by a 0.5-per cent trypsin solution is shown in Fig. 37 as a function of the time. With a solution so concentrated in enzyme, hydrolysis takes place extremely rapidly. It is interesting to note also the steady hydrolysis in the blank (without enzyme) at 40° C.

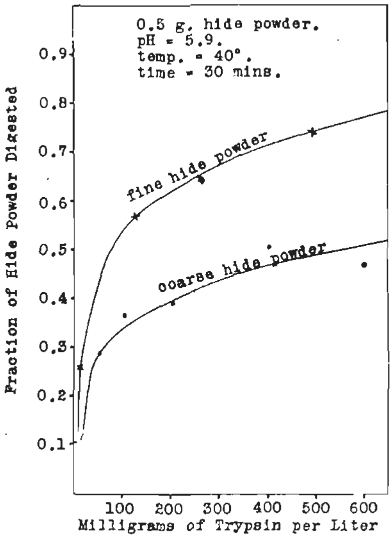


FIG. 38. Rates of digestion of fine and coarse hide powders as functions of the concentration of trypsin.

In Fig. 38 are shown the rates of digestion of fine and coarse hide powders as functions of the concentration of enzyme. The fine powder consisted of the portion passing through a sieve of 34 meshes to the inch and the coarse powder of the portion retained by the sieve. A much longer time is required to hydrolyze the coarse powder, as was expected. In Chapter 8 it will be shown that a concentrated solution of trypsin produces marked hydrolysis of calf skin only after acting for nearly 40 hours. Here the time required for diffusion of the enzyme into the skin and complications due to the presence of protein matter other than collagen play a part. In the method described above for preparing collagen for study, the action of the enzyme does not result in any very serious loss of collagen, but all of the elastin is digested.

Collagen is hydrolyzed by concentrated solutions of acids and alkalies in the cold, if sufficient time is allowed. Upon heating the solutions, the hydrolysis proceeds rapidly. In a study of the hydrolysis of gelatin by acids, alkalies, pepsin, and trypsin, Northrop[25] found that the course of the early stages of hydrolysis is similar with alkali, trypsin, and pepsin, but quite different with acid. He made a comparison of the relative velocities of hydrolysis of the various peptide linkings and observed the following important facts. Those linkages which are hydrolyzed by pepsin are also hydrolyzed by trypsin, but trypsin hydrolyzes linkages which are not attacked by pepsin. Of the linkages hydrolyzed by both enzymes, those most rapidly hydrolyzed

[25] Comparative Hydrolysis of Gelatin by Pepsin, Trypsin, Acid, and Alkali. J. H. Northrop. *J. General Physiol.* 4 (1921), 57.

by pepsin are only slowly attacked by trypsin. Those linkages which are most rapidly split by pepsin or trypsin are among the more resistant to acid hydrolysis and least resistant to hydrolysis by alkali.

The chemistry of collagen and gelatin forms so large a portion of the chemistry of leather manufacture that further treatment must be reserved for the appropriate chapters.

The skin contains a number of non-protein substances in the blood, lymph, and gland secretions. The blood and lymph contain sugars, salts, particularly the phosphates, carbonates, sulfates, and chlorides of sodium and potassium, and fatty matters, including cholesterols and the lecithins, which are phosphorous compounds of fats often existing in loose combination with proteins. Sodium chloride is the chief constituent of perspiration, which also contains sulfates, phosphates, and urea, and sometimes sebum. Sebum, the secretion of the sebaceous glands, consists of cholesterols, complex oleins, higher alcohols, and soaps, and is usually found contaminated with epithelial cells, probably those of the sebaceous glands furnishing the sebum.

Chapter 4.

Ionization of Acids and Bases Commonly Used in the Tannery.

Of vital importance in the use of tannery liquors is the control of hydrogen-ion and hydroxide-ion concentrations. Irregular variations in these concentrations are almost certain to result in corresponding irregularities in the properties of the leather produced. By juggling the methods of operation until a nearly uniform product was obtained and then rigidly adhering to a developed process, tanners long ago perfected means for keeping hydrogen-ion concentrations reasonably well under control, although without any appreciation as to why certain steps had to be followed. If liquors suddenly became infected with acid-producing ferments, or got beyond the control of the operator from other causes, the result was apt to be disastrous unless the tanner had learned from similar experiences how to correct the trouble.

Many of the pioneers who attempted to introduce chemical methods to the industry were handicapped by their inability to compare the activities of acids or bases of different strengths. Too much reliance upon the total concentration of acid, with little or no appreciation of its degree of ionization, has often proved very misleading. It is still not uncommon to find expensive acids being used where cheaper ones would serve the purpose as well or better. Even where an operator had come to appreciate that the determining factor was the hydrogen-ion concentration rather than the total titrable acidity, he was often without the means for determining hydrogen-ion concentrations and there were no easily available figures showing the degrees of ionization of the commoner acids and bases at different concentrations. In order to remedy this situation, Thomas [1] computed and compiled from the literature a series of tables showing the degrees of ionization of a number of acids and bases commonly used in the tannery; a range from 0.001 to 2 molar is covered. These tables are incorporated in this chapter because it is believed they will make certain portions of the book more readily comprehensible to a greater number of readers and will prove of great value for reference in experimental work on leather manufacture.

In making the calculations, Thomas used two modes of procedure. For the weak acids the concentrations of hydrogen ion have been cal-

[1] Tabulation of Hydrogen and Hydroxyl Ion Concentrations of Some Acids and Bases. A. W. Thomas. *J. Am. Leather Chem. Assoc.* 15 (1920), 133.

culated from the ionization constants (determined by conductivity measurements) by means of Ostwald's dilution law,

$$K = \frac{a^2}{V(1 - a)}$$

where K is the ionization constant, V the volume in which 1 gram molecular weight is dissolved, and *a* the degree of ionization. By rearrangement of the equation, we get

$$a = \frac{-KV + \sqrt{K^2V^2 + 4KV}}{2}$$

But, since the value of K^2V^2 is negligible compared to KV, it can be dropped for the purpose of making the calculations. The following expression, therefore, was used:

$$\text{Per cent ionization} = 100\sqrt{KV} - 50KV.$$

For the strong acids, the experimentally determined values for 100*a* at various concentrations were found in the literature. These were plotted against values for logV and a smooth curve was drawn through the points. The desired values were then read from the curve. The hydroxide-ion concentrations of bases were obtained similarly.

The figures in the tables may be in error as much as 5 per cent, especially in the cases of the strong acids and bases, but they are the best obtainable at this time. They were obtained from conductivity data and not from measurements by the hydrogen electrode.

Acids.

Acetic Acid.—Values calculated from the experimentally determined figures of Kendall.[2]

Boric Acid.—Calculated from $K = 6.6 \times 10^{-10}$ at 25° C. by Lunden.[3] 0.8 molar is saturated solution and since this acid is exceedingly weak, only the concentrations at 0.8, 0.1, 0.01, and 0.001 molar are given in the table.

Butyric Acid.—For concentrations 2 to 0.1 molar, calculated from $K = 1.49 \times 10^{-5}$ at 25° by Ostwald.[4] From 0.1 to 0.001 molar calculated from Ostwald's experimental values.

Carbonic Acid.—This acid is very weak and its concentration in solution depends upon the pressure of carbon dioxide on the surface of the solution. For this reason no special table was prepared and only two significant concentrations are given here, taken from Kendall.[5] At 25° the solubility of carbon dioxide in water at 1 atmosphere of pressure of carbon dioxide is 0.0337 mole per liter. The carbonic acid in this solution is 0.33 per cent ionized and hence its concentra-

[2] *Medd. Vetenskapsakad. Nobelinst.* Band 2, No. 38 (1913), 1-27.
[3] *J. chim. phys.* 5 (1907), 574.
[4] *Z. physik. Chem.* 3 (1889), 170.
[5] *J. Am. Chem. Soc.* 38 (1916), 1481.

tion of hydrogen ion is 0.00011 mole per liter, representing a pH value of 3.96. Under ordinary conditions, the partial pressure of carbon dioxide in the air is 0.000353 atmosphere, at which pressure carbon dioxide is soluble to the extent of 0.0000119 mole per liter, yielding a hydrogen-ion concentration of 0.000002 mole per liter or a pH value of 5.70.

Citric Acid.—For 2 to 0.4 molar, the values of Kendall, Booge and Andrews[6] are given. From 0.4 to 0.1 molar, the values are extrapolated. From 0.01 to 0.001 molar, the concentrations are calculated from the measurements of Walden.[7]

Formic Acid.—From 2 to 0.1 molar, the values are calculated from $K = 21.4 \times 10^{-5}$ at 25°, as given by Ostwald.[4] From 0.1 to 0.001 molar, they are calculated from Ostwald's experimental determinations.

Gallic Acid.—From 1 to 0.03 molar, values are calculated from $K = 4.0 \times 10^{-5}$, as given by Ostwald.[8] From 0.03 to 0.001 molar, values are calculated from Ostwald's experimental values.

Hydrochloric Acid.—The figures for 2 to 0.5 molar are from Jones.[9] Those for 0.5 to 0.001 molar are calculated from Kohlrausch's[10] experimentally determined values.

Lactic Acid.—The figures for 2 to 0.1 molar are based upon the figures of Kendall, Booge and Andrews;[6] those for 0.1 to 0.001 molar are calculated from the experimental values of Ostwald.[8]

Nitric Acid.—The 2 to 1 molar values are taken from Jones;[9] those for 0.5 to 0.001 molar are calculated from Kohlrausch's[10] data.

Oxalic Acid.—The only data available are those of Ostwald,[8] covering the range only from 0.03 to 0.004 molar. This acid is too highly ionized to permit calculations by the dilution law.

Phosphoric Acid.—Figures for 2 to 0.1 molar are calculated from the data of Kendall, Booge and Andrews;[6] those from 0.1 to 0.001 molar from the experimental data of Noyes and Eastman.[11]

Salicylic Acid.—Values are based upon the experimental data of Kendall.[2] 0.0167 molar represents the limit of solubility.

Sulfuric Acid.—The figures for 2 to 1 molar are from Jones;[9] those for 0.5 to 0.001 molar from the experimental data of Kohlrausch.[10]

Tartaric Acid.—From 2 to 0.04 molar, the figures are calculated from the data of Kendall, Booge and Andrews;[6] from 0.04 to 0.001 molar, they are calculated from Ostwald's[8] experimental data.

Bases.

Ammonium Hydroxide.—The figures for this weak base are calculated, by means of the dilution law, from $K = 1.8 \times 10^{-5}$ at 25° C., as given by Noyes, Kato and Sosman.[12]

Barium Hydroxide.—The only available data for this base are

[6] *J. Am. Chem. Soc.* 39 (1917), 2303.
[7] *Z. physik. Chem.* 10 (1892), 568.
[8] *Z. physik. Chem.* 3 (1889), 241.
[9] *Carnegie Inst. Publ.*, No. 60 (1907), 93.
[10] Morgan's Elements of Physical Chemistry, 4th edition (1908), 519.
[11] *Carnegie Inst. Publ.*, No. 63 (1907), 268.
[12] *Z. physik. Chem.* 73 (1910), 1.

those of Noyes and Eastman,[11] which range from 0.001 to 0.05 molar, upon which the calculations in the table are based.

Calcium Hydroxide.— No series of experimental data for this base could be found, but it is so similar to barium hydroxide that probably no great error would arise from the use of the barium hydroxide figures.

Potassium Hydroxide.—The 2 molar value is from Jones.[9] Values for 1 to 0.4 molar and from 0.03 to 0.001 molar are calculated from Kohlrausch's [10] data; those between 0.4 and 0.03 molar are obtained by extrapolation.

Sodium Hydroxide.—The 2 molar figure is from Jones;[9] the others are from Kohlrausch's [10] data.

Order of Strengths.

Listing the acids in order of increasing strength, or hydrogen-ion activities, we have

Boric
Carbonic
Butyric
Acetic
Gallic
Lactic
Formic
Citric
Tartaric
Salicylic
Phosphoric
Oxalic
Sulfuric
Nitric, Hydrochloric

Boric is the weakest acid in the list and hydrochloric and nitric are the strongest.

The bases in order of decreasing hydroxide-ion activity are

Potassium hydroxide
Sodium hydroxide
Barium hydroxide, Calcium hydroxide
Ammonium hydroxide

Temperature.

All of the values given in Tables II to X are for a temperature of 25° C. The temperature coefficient of ionization is small enough to be neglected for most practical purposes. The figures may, therefore, be considered valid for the range of temperature met with in the tannery.

pH Values.

The term pH value is now widely used to indicate the value of a, *with change of sign, in the expression* $[H^+] = 10^{-a}$ *moles per liter.* The use of this term has proved confusing to some because an increasing pH value indicates a decreasing hydrogen-ion concentration. But the pH scale has proved of great value for the operator with no knowledge of chemistry. He accepts it as a standard scale of acidity and alkalinity, as he does a thermometer for temperature, without caring about its mechanism. He learns, for example, that a given liquor works best at a pH value of 5.5. When the analyst reports to him a value for this liquor of 6.5, he immediately appreciates that the addition of acid is necessary to bring the liquor back to 5.5. The routine worker adopts the pH scale almost as easily as any other system

TABLE II.

Moles of acid per liter	Hydrochloric Acid			Nitric Acid		
	Per cent ionized	Moles H^+ per liter	pH value	Per cent ionized	Moles H^+ per liter	pH value
0.001	100.0	0.0010	3.00	100.0	0.0010	3.00
0.002	100.0	0.0020	2.70	99.5	0.0020	2.70
0.003	100.0	0.0030	2.52	99.5	0.0030	2.52
0.004	100.0	0.0040	2.40	99.4	0.0040	2.40
0.005	100.0	0.0050	2.30	99.4	0.0050	2.30
0.006	100.0	0.0060	2.22	99.4	0.0060	2.22
0.007	100.0	0.0070	2.15	99.3	0.0070	2.15
0.008	100.0	0.0080	2.10	99.3	0.0079	2.10
0.009	99.9	0.0090	2.05	99.3	0.0089	2.05
0.01	99.8	0.010	2.00	99.3	0.010	2.00
0.02	98.8	0.020	1.70	99.3	0.020	1.70
0.03	98.0	0.029	1.54	99.2	0.030	1.52
0.04	97.6	0.039	1.41	98.7	0.039	1.41
0.05	96.8	0.048	1.32	98.3	0.049	1.31
0.06	96.4	0.058	1.24	97.6	0.059	1.23
0.07	95.8	0.067	1.17	97.3	0.068	1.17
0.08	95.6	0.076	1.12	96.8	0.077	1.11
0.09	95.2	0.086	1.07	96.3	0.087	1.06
0.1	94.8	0.095	1.02	96.0	0.096	1.02
0.2	92.0	0.184	0.74	92.9	0.186	0.73
0.3	90.1	0.270	0.57	90.7	0.272	0.57
0.4	88.7	0.355	0.45	89.4	0.358	0.45
0.5	87.5	0.438	0.36	87.9	0.439	0.36
0.6	86.5	0.519	0.28	....	.....	....
0.7	84.7	0.593	0.23	....	.....	....
0.8	83.3	0.666	0.18	....	.....	....
0.9	81.5	0.734	0.13	....	.....	....
1.0	79.6	0.796	0.10	84.8	0.848	0.07
2.0	69.3	1.386	—0.14	73.9	1.478	—0.17

of measurement. He soon learns that pH = 7 represents a neutral solution, that values increasing from 7 indicate an increasing alkalinity and values decreasing from 7 an increasing acidity.

The investigator in leather chemistry finds it logical to plot variables against $-\log[H^+]$ rather than against actual hydrogen-ion concentrations because of the enormous range covered. For him the adoption of the pH scale has the advantage of eliminating the use of negative values and making his system of record conform to one more desirable for making plant reports, where the use of logarithms, negative values, and conceptions of ionization are often apt to lead to hopeless confusion.

The pH values corresponding to the various hydrogen-ion concentrations have been added to Thomas' tables in order to increase their usefulness.

TABLE III.

Moles of acid per liter	Sulfuric Acid *			Phosphoric Acid †		
	Per cent ionized	Moles H^+ per liter	pH value	Per cent ionized	Moles H^+ per liter	pH value
0.001	97.7	0.0020	2.70	89.0	0.0009	3.05
0.002	94.7	0.0038	2.42	83.0	0.0017	2.77
0.003	90.5	0.0054	2.27	77.5	0.0023	2.64
0.004	88.0	0.0070	2.15	73.5	0.0029	2.54
0.005	85.9	0.0086	2.07	70.0	0.0035	2.46
0.006	84.2	0.0101	2.00	67.5	0.0041	2.39
0.007	82.7	0.0116	1.94	65.0	0.0046	2.34
0.008	81.8	0.0131	1.88	63.0	0.0050	2.30
0.009	80.5	0.0145	1.84	60.5	0.0054	2.27
0.01	79.6	0.016	1.80	59.0	0.006	2.23
0.02	73.1	0.029	1.54	47.5	0.010	2.00
0.03	69.4	0.042	1.38	42.0	0.013	1.89
0.04	66.8	0.053	1.28	38.0	0.015	1.82
0.05	64.8	0.065	1.19	35.0	0.018	1.74
0.06	63.5	0.076	1.12	33.0	0.020	1.70
0.07	62.4	0.087	1.06	31.0	0.022	1.66
0.08	61.7	0.099	1.00	30.0	0.024	1.62
0.09	61.1	0.110	0.96	28.5	0.026	1.58
0.1	60.7	0.121	0.92	27.5	0.028	1.55
0.2	57.6	0.230	0.64	22.8	0.046	1.34
0.3	56.0	0.336	0.47	20.7	0.062	1.21
0.4	54.7	0.438	0.36	19.8	0.079	1.10
0.5	53.6	0.536	0.27	19.0	0.095	1.02
0.6	52.9	0.635	0.20	18.8	0.113	0.95
0.7	52.0	0.728	0.14	18.0	0.126	0.90
0.8	51.4	0.822	0.09	17.9	0.143	0.84
0.9	50.9	0.916	0.04	17.7	0.159	0.80
1.0	50.7	1.014	—0.01	17.5	0.175	0.76
2.0	39.9	1.596	—0.20	16.1	0.322	0.49

* 100 per cent ionization taken as complete ionization into H^+, H^+, and SO_4''.
† 100 per cent ionization taken as complete ionization into H^+ and H_2PO_4'.

TABLE IV.

Moles of acid per liter	Formic Acid Per cent ionized	Formic Acid Moles H^+ per liter	Formic Acid pH value	Acetic Acid Per cent ionized	Acetic Acid Moles H^+ per liter	Acetic Acid pH value
0.001	35.8	0.00036	3.44	12.8	0.00013	3.89
0.002	27.1	0.00054	3.27	9.2	0.00018	3.74
0.003	22.0	0.00066	3.18	7.5	0.00023	3.64
0.004	20.1	0.00080	3.10	6.6	0.00026	3.58
0.005	18.0	0.00090	3.05	5.9	0.00030	3.52
0.006	16.6	0.00100	3.00	5.4	0.00032	3.49
0.007	15.5	0.00109	2.96	5.0	0.00035	3.46
0.008	14.8	0.00118	2.93	4.7	0.00038	3.42
0.009	14.0	0.00126	2.90	4.4	0.00040	3.40
0.01	13.4	0.0013	2.87	4.2	0.00042	3.38
0.02	9.7	0.0019	2.72	3.0	0.00060	3.22
0.03	8.1	0.0024	2.62	2.4	0.00072	3.14
0.04	7.1	0.0028	2.55	2.1	0.00084	3.08
0.05	6.4	0.0032	2.49	1.9	0.00095	3.02
0.06	5.8	0.0035	2.46	1.7	0.00102	2.99
0.07	5.4	0.0038	2.42	1.55	0.00109	2.96
0.08	5.0	0.0040	2.40	1.5	0.00120	2.92
0.09	4.7	0.0042	2.38	1.4	0.00126	2.90
0.1	4.5	0.0045	2.35	1.3	0.00130	2.89
0.2	3.2	0.0064	2.19	0.9	0.00180	2.74
0.3	2.6	0.0078	2.11	0.7	0.00210	2.68
0.4	2.3	0.0092	2.04	0.6	0.00240	2.62
0.5	2.1	0.0105	1.98	0.57	0.00285	2.55
0.6	1.9	0.0114	1.94	0.50	0.00300	2.52
0.7	1.8	0.0126	1.90	0.45	0.00315	2.50
0.8	1.7	0.0136	1.87	0.42	0.00336	2.47
0.9	1.6	0.0144	1.84	0.40	0.00360	2.44
1.0	1.5	0.0150	1.82	0.37	0.00370	2.43
2.0	1.03	0.0206	1.69	0.30	0.00600	2.22

TABLE V.

Moles of acid per liter	Gallic Acid			Lactic Acid		
	Per cent ionized	Moles H^+ per liter	pH value	Per cent ionized	Moles H^+ per liter	pH value
0.001	18.7	0.00019	3.72	30.9	0.00031	3.51
0.002	13.4	0.00027	3.57	23.0	0.00046	3.34
0.003	10.7	0.00032	3.49	18.7	0.00056	3.25
0.004	9.3	0.00037	3.43	16.7	0.00067	3.18
0.005	8.4	0.00042	3.38	15.1	0.00076	3.12
0.006	7.6	0.00046	3.34	13.9	0.00083	3.08
0.007	7.0	0.00049	3.31	12.9	0.00090	3.05
0.008	6.7	0.00054	3.27	12.2	0.00098	3.01
0.009	6.2	0.00056	3.25	11.5	0.00104	2.98
0.01	5.9	0.00059	3.23	11.0	0.00110	2.96
0.02	4.1	0.00082	3.09	8.0	0.00160	2.80
0.03	3.3	0.00099	3.00	6.6	0.00198	2.70
0.04	3.0	0.00120	2.92	5.8	0.00232	2.63
0.05	2.70	0.00135	2.87	5.2	0.00260	2.58
0.06	2.50	0.00150	2.82	4.8	0.00288	2.54
0.07	2.30	0.00161	2.79	4.3	0.00301	2.52
0.08	2.20	0.00176	2.75	4.1	0.00328	2.48
0.09	2.05	0.00185	2.73	3.8	0.00342	2.47
0.1	1.98	0.0020	2.70	3.7	0.00370	2.43
0.2	1.40	0.0028	2.55	2.7	0.0054	2.27
0.3	1.15	0.0035	2.46	2.2	0.0066	2.18
0.4	1.00	0.0040	2.40	1.8	0.0072	2.14
0.5	0.89	0.0045	2.35	1.6	0.0080	2.10
0.6	0.80	0.0048	2.32	1.5	0.0090	2.05
0.7	0.74	0.0052	2.28	1.4	0.0098	2.01
0.8	0.70	0.0056	2.25	1.3	0.0104	1.98
0.9	0.68	0.0061	2.21	1.2	0.0108	1.97
1.0	0.63	0.0063	2.20	1.1	0.0110	1.96
2.0	....	......	....	0.8	0.0160	1.80

TABLE VI.

Moles of acid per liter	Butyric Acid: Per cent ionized	Butyric Acid: Moles H^+ per liter	Butyric Acid: pH value	Boric Acid*: Per cent ionized	Boric Acid*: Moles H^+ per liter	Boric Acid*: pH value
0.001	11.4	0.00011	3.96	0.080	0.0000008	6.10
0.002	8.3	0.00017	3.77	.....	.....	....
0.003	6.8	0.00020	3.70	.....	.....	....
0.004	6.0	0.00024	3.62	.....	.....	....
0.005	5.4	0.00027	3.57	.....	.....	....
0.006	4.9	0.00029	3.54	.....	.....	....
0.007	4.55	0.00032	3.49	.....	.....	....
0.008	4.3	0.00034	3.47	.....	.....	....
0.009	3.95	0.00036	3.44	.....		
0.01	3.8	0.00038	3.42	0.026	0.0000026	5.58
0.02	2.7	0.00054	3.27	.....	.....	....
0.03	2.2	0.00066	3.18	.....	.....	....
0.04	1.95	0.00078	3.11	.....	.....	....
0.05	1.7	0.00085	3.07	.....	.....	....
0.06	1.6	0.00096	3.02	.....	.....	....
0.07	1.4	0.00098	3.01	.....	.....	....
0.08	1.35	0.00108	2.97	.....	.....	....
0.09	1.25	0.00113	2.95	.....		
0.1	1.2	0.00120	2.92	0.008	0.0000080	5.10
0.2	0.86	0.00172	2.76	.....	.....	....
0.3	0.70	0.00210	2.68	.....	.....	....
0.4	0.60	0.00240	2.62	.....	.....	....
0.5	0.54	0.00270	2.57	.....	.....	....
0.6	0.49	0.00294	2.53	.....	.....	....
0.7	0.43	0.00301	2.52	.....	.....	....
0.8	0.41	0.00328	2.48	0.003	0.0000240	4.62
0.9	0.40	0.00360	2.44	.....	.....	....
1.0	0.39	0.00390	2.40	.....	.....	....
2.0	0.27	0.00540	2.27	.....	.....	....

* 100 per cent ionization taken as complete ionization into H^+ and H_2BO_3'.

TABLE VII.

Moles of acid per liter	Tartaric Acid *			Citric Acid †		
	Per cent ionized	Moles H^+ per liter	pH value	Per cent ionized	Moles H^+ per liter	pH value
0.001	65.3	0.0007	3.15	60.2	0.0006	3.22
0.002	51.0	0.0010	3.00	47.4	0.0009	3.05
0.003	43.0	0.0013	2.89	39.8	0.0012	2.92
0.004	39.0	0.0016	2.80	36.0	0.0014	2.85
0.005	35.5	0.0018	2.74	33.1	0.0017	2.77
0.006	33.0	0.0020	2.70	30.8	0.0018	2.74
0.007	31.0	0.0022	2.66	28.9	0.0020	2.70
0.008	30.0	0.0024	2.62	27.6	0.0022	2.66
0.009	28.0	0.0025	2.60	25.9	0.0023	2.64
0.01	27.0	0.0027	2.57	25.0	0.0025	2.60
0.02	19.5	0.0039	2.41	18.3	0.0037	2.43
0.03	16.5	0.0050	2.30	15.5	0.0047	2.33
0.04	14.5	0.0058	2.24	13.8	0.0055	2.26
0.05	13.1	0.0066	2.18	12.5	0.0063	2.20
0.06	12.2	0.0073	2.14	11.5	0.0069	2.16
0.07	11.4	0.0080	2.10	10.7	0.0075	2.12
0.08	10.9	0.0087	2.06	10.1	0.0081	2.09
0.09	10.2	0.0092	2.04	9.5	0.0086	2.07
0.1	9.9	0.010	2.00	9.1	0.009	2.04
0.2	7.1	0.014	1.85	6.1	0.012	1.92
0.3	5.7	0.017	1.77	4.7	0.014	1.85
0.4	4.9	0.020	1.70	4.0	0.016	1.80
0.5	4.2	0.021	1.68	3.5	0.018	1.74
0.6	3.7	0.022	1.66	3.1	0.019	1.72
0.7	3.5	0.025	1.60	3.0	0.021	1.68
0.8	3.2	0.026	1.58	2.9	0.023	1.64
0.9	3.0	0.027	1.57	2.8	0.025	1.60
1.0	2.9	0.029	1.54	2.7	0.027	1.57
2.0	2.1	0.042	1.38	1.8	0.036	1.44

* 100 per cent ionization taken as complete ionization into H^+ and $HC_4H_4O_6'$.
† 100 per cent ionization taken as complete ionization into H^+ and $H_2C_6H_5O_7'$.

TABLE VIII.

Moles of acid per liter	Oxalic Acid * Per cent ionized	Moles H^+ per liter	pH value	Salicylic Acid Per cent ionized	Moles H^+ per liter	pH value
0.001	....	......	....	62.0	0.0006	3.22
0.002	....	......	....	51.0	0.0010	3.00
0.003	....	......	....	44.5	0.0013	2.89
0.004	95.0	0.0038	2.42	40.0	0.0016	2.80
0.005	93.0	0.0047	2.33	37.0	0.0019	2.72
0.006	91.5	0.0055	2.26	34.5	0.0021	2.68
0.007	90.0	0.0063	2.20	32.0	0.0022	2.66
0.008	89.0	0.0071	2.15	30.5	0.0024	2.62
0.009	88.0	0.0079	2.10	29.0	0.0026	2.58
0.010	87.0	0.0087	2.06	27.7	0.0028	2.55
0.0167	....	......	....	24.0	0.0040	2.40
0.020	79.0	0.0158	1.80	....	......	....
0.030	73.5	0.0221	1.66	....	......	....

* 100 per cent ionization taken as complete ionization into H^+ and HC_2O_4'.

TABLE IX.

Moles of base per liter	Potassium Hydroxide Per cent ionized	Moles OH' per liter	pH value	Sodium Hydroxide Per cent ionized	Moles OH' per liter	pH value
0.001	100.0	0.001	11.00	100.00	0.001	11.00
0.002	100.0	0.002	11.30	100.0	0.002	11.30
0.003	100.0	0.003	11.48	100.0	0.003	11.48
0.004	100.0	0.004	11.60	100.0	0.004	11.60
0.005	100.0	0.005	11.70	100.0	0.005	11.70
0.006	100.0	0.006	11.78	100.0	0.006	11.78
0.007	100.0	0.007	11.85	100.0	0.007	11.85
0.008	100.0	0.008	11.90	99.9	0.008	11.90
0.009	99.9	0.009	11.95	99.7	0.009	11.95
0.01	99.9	0.010	12.00	99.5	0.010	12.00
0.02	99.3	0.020	12.30	97.9	0.020	12.30
0.03	98.7	0.030	12.48	96.8	0.029	12.46
0.04	97.9	0.039	12.59	96.0	0.038	12.58
0.05	97.3	0.049	12.69	95.3	0.048	12.68
0.06	96.7	0.058	12.76	94.7	0.057	12.76
0.07	96.2	0.067	12.83	94.1	0.066	12.82
0.08	95.8	0.077	12.89	93.7	0.075	12.88
0.09	95.3	0.086	12.93	93.2	0.084	12.92
0.1	95.0	0.095	12.98	92.9	0.093	12.97
0.2	92.2	0.184	13.26	89.8	0.180	13.26
0.3	90.1	0.270	13.43	87.0	0.261	13.42
0.4	88.8	0.355	13.55	85.3	0.341	13.53
0.5	87.6	0.438	13.64	83.5	0.418	13.62
0.6	86.3	0.518	13.71	81.9	0.491	13.69
0.7	85.0	0.595	13.77	80.4	0.563	13.75
0.8	84.3	0.674	13.83	79.2	0.634	13.80
0.9	82.8	0.745	13.87	77.7	0.699	13.84
1.0	81.9	0.819	13.91	76.6	0.766	13.88
2.0	66.3	1.326	14.12	57.0	1.140	14.06

TABLE X.

Moles of base per liter	Ammonium Hydroxide			Barium Hydroxide *		
	Per cent ionized	Moles OH' per liter	pH value	Per cent ionized	Moles OH' per liter	pH value
0.001	12.52	0.00013	10.11	96.0	0.0010	11.00
0.002	8.99	0.00018	10.26	95.0	0.0019	11.28
0.003	7.44	0.00022	10.34	94.0	0.0028	11.45
0.004	6.48	0.00026	10.42	93.0	0.0037	11.57
0.005	5.82	0.00029	10.46	92.0	0.0046	11.66
0.006	5.33	0.00032	10.51	91.3	0.0055	11.74
0.007	4.93	0.00035	10.54	91.0	0.006	11.78
0.008	4.62	0.00037	10.57	90.5	0.007	11.85
0.009	4.37	0.00039	10.59	90.0	0.008	11.90
0.01	4.15	0.00042	10.62	88.4	0.009	11.95
0.02	2.96	0.00059	10.77	86.0	0.017	12.23
0.03	2.42	0.00073	10.86	82.8	0.025	12.40
0.04	2.12	0.00085	10.93	81.0	0.032	12.51
0.05	1.88	0.00094	10.97	80.0	0.040	12.60
0.06	1.72	0.00103	11.01	....	.....	.....
0.07	1.59	0.00111	11.05	....	.....	.....
0.08	1.49	0.00119	11.08	....	.....	.....
0.09	1.40	0.00126	11.10	....	.....	.....
0.1	1.33	0.00133	11.12	....	.....	.....
0.2	0.94	0.00188	11.27	....	.....	.....
0.3	0.77	0.00231	11.36	....	.....	.....
0.4	0.67	0.00268	11.43	....	.....	.....
0.5	0.60	0.00300	11.48	....	.....	.....
0.6	0.55	0.00330	11.52	....	.....	.....
0.7	0.50	0.00350	11.54	....	.....	.....
0.8	0.47	0.00376	11.58	....	.....	.....
0.9	0.45	0.00405	11.61	....	.....	.....
1.0	0.42	0.00420	11.62	....	.....	.....
2.0	0.30	0.00600	11.78	....	.....	.....

* 100 per cent ionization taken as complete ionization into $BaOH^+$ and OH'.

NOTE: Where figures for calcium hydroxide are desired, it is suggested that those for barium hydroxide be used.

Effect of Added Salts.

The figures given in the tables are for pure solutions of the acids or bases. The addition of sodium chloride, or other neutral chlorides, tends to increase the hydrogen-ion concentrations of acids[13 14 15 16] and the hydroxide-ion concentration of bases.[14] Neutral sulfates, on the other hand, tend to decrease the hydrogen-ion concentrations of acids.

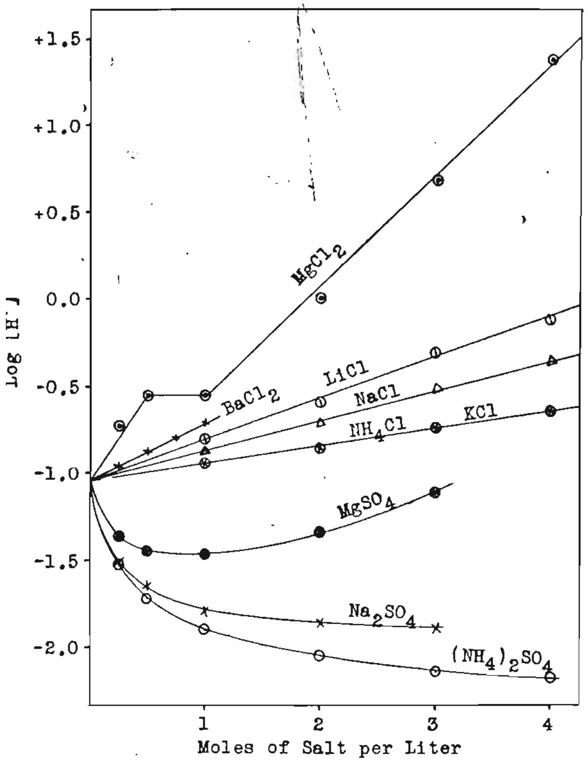


FIG. 39.—Effect of concentration of various salts upon the hydrogen-ion concentration of tenth-normal hydrochloric acid solution.

This contrasting effect of chlorides and sulfates on the hydrogen-ion concentrations of solutions of sulfuric and hydrochloric acids was shown by Thomas and Baldwin.[17] Their results for 0.1 normal acids are shown in Figs. 39 and 40. In each case a solution of acid was

[13] Poma, *Z. physik. Chem.* 88 (1914), 671.
[14] Harned, *J. Am. Chem. Soc.* 37 (1915), 2460.
[15] Fales and Nelson, *ibid.*, 37 (1915), 2769.
[16] Thomas and Baldwin, *J. Am. Leather Chem. Assoc.* 13 (1918), 248.
[17] Contrasting Effects of Chlorides and Sulfates on the Hydrogen-Ion Concentrations of Acid Solutions. A. W. Thomas and M. E. Baldwin. *J. Am. Chem. Soc.* 41 (1919), 1981.

mixed with a solution of salt and diluted to 100 cubic centimeters so that the final concentration of acid was 0.1 normal and that of the salt the concentration whose effect was being studied. The hydrogen-ion concentrations were measured, by means of the hydrogen electrode, two days after the solutions were made up.

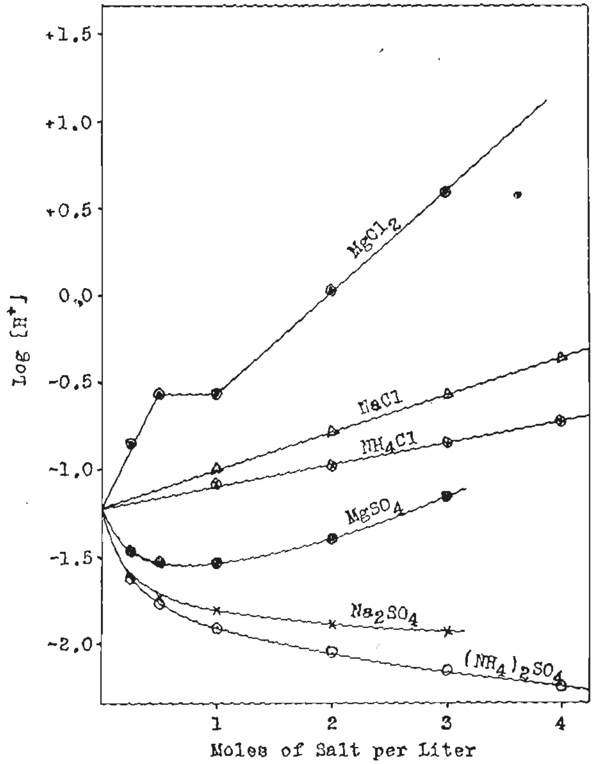


FIG. 40.—Effect of concentration of various salts upon the hydrogen-ion concentration of tenth-normal sulfuric acid solution.

When the chlorides are arranged in order of their ability to increas the hydrogen-ion concentration, the following series is obtained:

$$KCl \approx NH_4Cl < NaCl < LiCl < BaCl_2 < MgCl_2$$

But this is also the order of increasing degree of hydration, or tl number of molecules of water combined with the individual cations infinite dilution. Poma[13] found that chlorides increase the hydroge ion concentrations of hydrochloric acid solutions in the followi order:

$$RbCl < KCl < LiCl < CaCl_2 < MgCl_2$$

In extending the work of Thomas and Baldwin, Wilson [18] pointed out that one of the remarkable features of their results is that when the logarithm of the concentration of hydrogen ion is plotted against the concentration of added salt, in the case of the alkali chlorides, the curves are apparently straight lines, of the general formula

$$\log [H^+] = \log a + bm$$

where *b* is a constant, *a* the hydrogen-ion concentration when no salt

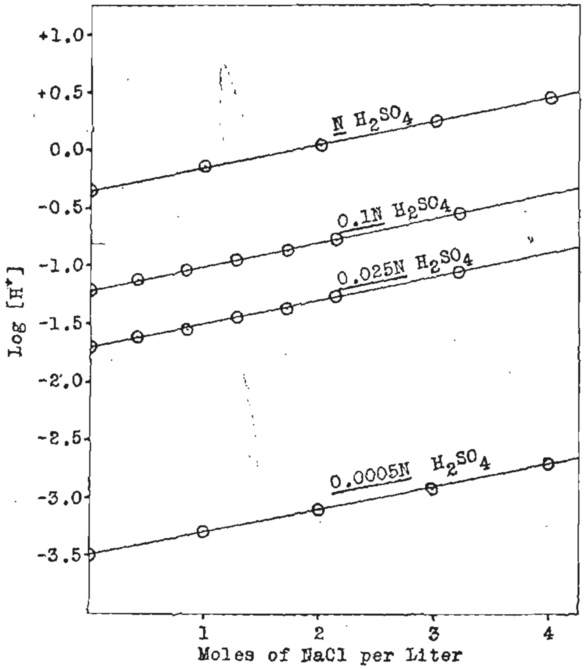


FIG. 41.—Effect of concentration of sodium chloride upon the hydrogen-ion concentration of various strengths of sulfuric acid solution.

is present, and $[H^+]$ the hydrogen-ion concentration in the presence of *m* moles per liter of salt.

It was also shown that this equation is independent of the strength of the acid solution, the value for *b* depending only upon the kind of alkali chloride added. Curves showing the effect of adding sodium chloride to four different concentrations of sulfuric acid are shown in Fig. 41. Apparently the curves are not only straight lines, but all four have the same slope, the average value for *b* being 0.205.

The addition of 4 moles per liter of sodium chloride raises the hydrogen-ion concentration of 0.1 molar hydrochloric acid to 0.44

[18] Hydration as an Explanation of the Neutral Salt Effect. J. A. Wilson. *J. Am. Chem. Soc.* 42 (1920), 715.

mole per liter, which can be accounted for only on the assumption that more than three-quarters of the water present has ceased to play the rôle of solvent. The hydration theory assumes that this is brought about by the water combining with the salt.

If the rise in hydrogen-ion concentration is due to the removal of water by the added sodium chloride, it should be possible to determine the degree of hydration of the salt at any concentration from hydrogen-ion measurements. Assuming this to be so, we should reason as follows: From the above equation, $\log([H^+]/a) = bm$. But $[H^+]/a$ is the factor by which the acid concentration has been multiplied by adding *m* moles per liter of salt. Let *w* represent the total number of moles of water, free or combined with salt, in 1 liter of solution containing *m* moles of salt. The moles of free water then equal $wa/[H^+]$ and the moles of water combined with one mole of salt equal $(w/m) \times (1 - a/[H^+])$. Calling this latter value *h*, we have

$$h = w(1 - 10^{-bm})/m.$$

From this, hydration values can be calculated for any concentration of salt. For infinite dilution of salt, the expression becomes greatly simplified, for

$$\lim_{m = 0} (1 - 10^{-bm})/m = 2.30b.$$

But at infinite dilution $w = 55.5$ and hence

$$h = 128b.$$

The calculated number of molecules of water combined with one molecule of sodium chloride at infinite dilution would thus be 128×0.205 or 26.2, which is in striking agreement with the value 26.5 obtained by Smith[19] from a very different type of measurement. Calculations of the degrees of hydration at infinite dilution of the chlorides of potassium, ammonium, and lithium made from the equation $h = 128b$ also agreed fairly well with Smith's corresponding values.

A means is thus afforded to calculate the change of pH value that will be produced by the addition of a neutral chloride to an acid solution. Let I represent the pH value of the acid solution containing no salt, which may be found in the preceding tables. Let F be the pH value after the addition of *m* moles per liter of salt and H be the number of molecules of water combined with one molecule of salt at infinite dilution. Then

$$F = I - 0.0078Hm.$$

The use of this equation does not depend upon the validity of the theory. The measurements of Thomas and Baldwin show that it may be used for the addition of chlorides to sulfuric and hydrochloric acids by substituting the following values for H:

[19] A Method for the Calculation of the Hydration of the Ions at Infinite Dilution. G. McP. Smith. *J. Am. Chem. Soc.* 37 (1915), 722.

potassium chloride	15
ammonium chloride	15
sodium chloride	26
lithium chloride	35
barium chloride	50

The effect of adding sulfates cannot, however, be attributed to hydration, since they decrease the hydrogen-ion concentrations of acid solutions. Their action is probably due to the formation of addition compounds complicated by hydration effects. For the hydrogen-ion concentrations of sulfuric and hydrochloric acid solutions containing neutral sulfates, reference should be made to the original papers of Thomas and Baldwin.

For the degrees of ionization of a large number of different salts at various concentrations, the reader is referred to page 35 of the recent book of Kraus.[20]

A skin is subjected to liquors of widely different pH value in passing through the tannery. From a lime liquor having a pH value of 12.5 it may pass into a bate liquor with a pH value of 7.5, then into a pickle liquor of pH = 1.5, then into a chrome liquor whose pH value is rising from 3 to 4, and then into a fat liquor at pH = 9. Or, in vegetable tanning, the skin may pass from the bate liquor to a tan liquor whose pH value may be anything from 2.5 to 5.5, depending upon the method of operation of the yards. But in spite of the wide variation in pH value to which the skin is subjected in passing through the tannery, the processes are all sensitive to comparatively small variations in pH value unless each variation is compensated by corresponding changes in the process itself.

[20] The Properties of Electrically Conducting Systems. C. A. Kraus. Chemical Catalog Co., New York.

Chapter 5.

Physical Chemistry of the Proteins.

The physical chemistry of the proteins is one of the foundations upon which leather chemistry is built, but until comparatively recently our knowledge of the chemical reactions of the proteins was hardly sufficient to permit of quantitative treatment. Proteins did not seem to show the stoichiometric relations of orthodox physical chemistry to earlier investigators because they failed to recognize the full number of phases existing in a given system and the necessity for making measurements at definite hydrogen-ion concentrations.

The way for the quantitative development of the physical chemistry of the proteins was paved by the appearance of Donnan's theory of membrane equilibria,[1] which was applied by Procter [2] to the swelling of gelatin and further developed by Procter and Wilson [3] into a quantitative theory of the swelling of protein jellies. In an extensive series of researches, Loeb [4] has extended this work to include also the osmotic pressure, viscosity, stability, and electrical potential differences of protein systems as well as a general theory of colloidal behavior. This valuable work is now available in book form [5] and should be consulted as having an important bearing upon leather chemistry.

It will be shown in this chapter that proteins conform to the classical laws of physical chemistry and that their reactions are indicated by well established principles. Donnan's theory forms the logical starting point for this presentation. A good discussion of Donnan's theory is given in Lewis' Physical Chemistry; [6] we have extended it in this chapter to a consideration of the effects of valency.

Donnan's Theory of Membrane Equilibria.

This theory deals with the equilibria resulting from the separation by a membrane of two solutions, one of which contains an ionogen having one ion that cannot diffuse through the membrane, which is permeable to all other ions of the system. As an example, Donnan

[1] F. G. Donnan. *Z. Elektrochem.* 17 (1911), 572.
[2] Equilibrium of Dilute Hydrochloric Acid and Gelatin. H. R. Procter. *J. Chem. Soc.* 105 (1914), 313.
[3] The Acid-Gelatin Equilibrium. H. R. Procter and J. A. Wilson. *J. Chem. Soc.* 109 (1916), 307.
[4] *J. General Physiol.*, 1918-1922.
[5] Proteins and the Theory of Colloidal Behavior. Jacques Loeb. McGraw-Hill Book Co., New York.
[6] A System of Physical Chemistry, Vol. II, Thermodynamics, pp. 275-86. Longmans, Green & Co., London.

takes an aqueous solution of a salt NaR, such as Congo red, in contact with a membrane which is impermeable to the anion R′ and the non-ionized salt, but will allow Na^+ or any other ion to pass freely through it. The membrane separates the Congo red solution from an aqueous solution of sodium chloride, which will diffuse from its Solution II into the Solution I of NaR. When equilibrium is established, if a small virtual change is made reversibly at constant temperature and volume, the free energy will remain unchanged; that is, no work will be done. The change here considered is the transfer of *dn* moles of Na^+ and Cl′ from II to I. The work, which equals zero, is

$$dn.\mathrm{RT}.\log\frac{[\mathrm{Na}^+]_{\mathrm{II}}}{[\mathrm{Na}^+]_{\mathrm{I}}} + dn.\mathrm{RT}.\log\frac{[\mathrm{Cl}']_{\mathrm{II}}}{[\mathrm{Cl}']_{\mathrm{I}}} = 0,$$

whence $$[\mathrm{Na}^+]_{\mathrm{II}} \times [\mathrm{Cl}']_{\mathrm{II}} = [\mathrm{Na}^+]_{\mathrm{I}} \times [\mathrm{Cl}']_{\mathrm{I}}.$$

(The brackets indicate concentration in moles per liter.)

Equilibrium will be established only when the product of the concentrations of Na^+ and Cl′ has the same value on both sides of the membrane.

This equation of products, simple though it may appear, is of such fundamental importance in the quantitative development of leather chemistry that any doubt as to its validity should be dispelled at the outset. The derivation of the equation need not involve the use of thermodynamics, since it can readily be visualized. In passing from one phase to the other, the oppositely charged ions must move in pairs, since they would otherwise set up powerful electrostatic forces that would prevent their free diffusion. For this reason a sodium or a chlorine ion striking the membrane alone could not pass through it. But, since the membrane is freely permeable to both Na^+ and Cl′, when two oppositely charged ions strike the membrane together, there is nothing to prevent them from passing through into the solution on the opposite side. The rate of transfer of these ions from one solution to the other depends, therefore, upon the frequency with which they chance to strike the membrane in pairs, which is measured by the product of their concentrations. At equilibrium the rate of transfer of Na^+ and Cl′ from Solution II to Solution I exactly equals the rate of transfer of these ions from Solution I to Solution II, from which it follows that the product of the concentrations of these ions has the same value in both solutions.

It is interesting now to note the effect of complicating the system by the introduction of another salt, such as KBr. Following the same line of reasoning, it will be evident that equilibrium will be established only when the product $[K^+] \times [Br']$ has the same value in both solutions, and the same is true for the products $[K^+] \times [Cl']$ and $[Na^+] \times [Br']$. In fact, with any number of mono-monovalent ionogens present in the system, the product of the concentrations of any pair of diffusible and oppositely charged ions will have the same value in both solutions.

Introducing polyvalent ions into the system makes the equation

of products but very little more complicated. When a polyvalent ion strikes the membrane, it will pass through only when an equivalent number of ions of opposite sign strike the membrane at the same time and pass through with it. The rate of transfer of any dissociated ionogen from one solution to the other is evidently determined by the product of all the ions required to produce the undissociated ionogen. At equilibrium, this product will have the same value in both solutions. If, for example, the system contained the ions Na^+ and SO''_4, then the product $[Na^+] \times [Na^+] \times [SO''_4]$, or $[Na^+]^2 \times [SO''_4]$, would have the same value on both sides of the membrane, at equilibrium.

The impermeability of the membrane to the anion R′ causes an unequal distribution of ions between the two solutions. In Solution II of the simple system including only the ionogens NaR and NaCl, let

$$x = [Na^+] = [Cl'].$$

In Solution I let $\quad y = [Cl']$

and $\quad z = [R']$

whereupon $\quad [Na^+] = y + z.$

The equation of products may then be written

$$x^2 = y(y + z).$$

But here we have the product of equals equated to the product of unequals, from which it is apparent, mathematically, that the sum of the unequals is greater than the sum of the equals, or that

$$2y + z > 2x.$$

The reasoning thus indicates that the concentration of diffusible ions in Solution I, at equilibrium, is greater than in Solution II, and this has been shown to be true in numerous experiments. If we let the excess of diffusible ions of Solution I over Solution II be represented by *e*, then $\quad 2y + z = 2x + e,$

or $\quad x = y + \sqrt{ey},$

which shows us further that x is greater than y or that the concentration of ionized sodium chloride is greater in Solution II than in Solution I. The added sodium chloride does not distribute itself equally throughout both solutions, but, at equilibrium, it is the more concentrated in Solution II.

The different distribution of ions in the solutions at equilibrium gives rise, not only to a difference in osmotic pressure, but also to an electrical difference of potential across the membrane. Donnan derived the equation for this potential difference by the following thermodynamic reasoning.

In the system just described, let π_I be the potential, for positive electricity, of solution I and π_{II} that for Solution II. Let the ex-

tremely small quantity Fdn of positive electricity be transferred isothermally from II to I. In this virtual change of the system from equilibrium, the following work terms must be considered: the change in free electrical energy represented by $Fdn\ (\pi_{II} - \pi_I)$ and the simultaneous transfer of pdn moles of Na^+ from II to I and of qdn moles of Cl' from I to II, where p and q are the respective transport numbers of the ions, and hence $p + q = 1$. The maximum osmotic work of operation of this transfer of ions is represented by the expression

$$pdnRT.\log \frac{[Na^+]_{II}}{[Na^+]_I} + qdnRT.\log \frac{[Cl']_I}{[Cl']_{II}}$$

But, since the system is in equilibrium, the electrical virtual work must balance the osmotic virtual work, or

$$Fdn\ (\pi_I - \pi_{II}) = pdnRT.\log \frac{[Na^+]_{II}}{[Na^+]_I} + qdnRT.\log \frac{[Cl']_I}{[Cl']_{II}}$$

But $\frac{[Na^+]_{II}}{[Na^+]_I} = \frac{[Cl']_I}{[Cl']_{II}} = \frac{x}{y}$ and $p + q = 1$. Letting $E = \pi_I - \pi_{II}$, we have

$$E = \frac{RT}{F} \log \frac{x}{y} \text{ volts.}$$

This is an equation of fundamental importance in the theory of the mechanism of many reactions involved in leather making.

It will now be shown that this equation is still valid when other ions of any valency are added to the system. Consider the general case where an ionogen yielding the ion M^{a+} of valency a is added. By applying the above line of reasoning to the potential difference produced by the unequal distribution of the ions of the added ionogen between solutions I and II, we arrive at the equation

$$E = \frac{RT}{nF}.\log \frac{[M^{a+}]_{II}}{[M^{a+}]_I}$$

where $n = a$, the valency of M^{a+}. But it is evident from the equation of products that

$$[M^{a+}]_I \times [Cl']^a_I = [M^{a+}]_{II} \times [Cl']^a_{II}$$

and that $\quad [Na^+]^a_I \times [Cl']^a_I = [Na^+]^a_{II} \times [Cl']^a_{II}$

from which it is apparent that

$$\frac{[M^{a+}]_{II}}{[M^{a+}]_I} = \frac{[Na^+]^a_{II}}{[Na^+]^a_I} = \frac{x^a}{y^a}$$

Therefore

$$E = \frac{RT}{aF}.\log \frac{x^a}{y^a} = \frac{RT}{F}.\log \frac{x}{y}$$

the fact that the membrane prevents the diffusion of one kind of ion from one phase to the other. A similar set of conditions is brought about whenever one of a number of ions of a system is prevented from diffusing from one phase to another, which is true for every basic tannery process. When skin protein is brought into equilibrium with various tannery liquors, the diffusion of the protein ions is prevented, not by a membrane, but by their own forces of cohesion. This will be made clear in discussing the swelling of proteins.

Swelling of Protein Jellies.

When a strip of dry gelatin is soaked in water, it swells by absorbing water, increasing in volume from 5 to 10 times, depending upon the temperature of the water and the quality of the gelatin. With increasing concentration of acid, or alkali, the swelling increases to a maximum and then decreases. The property of swelling in aqueous solutions appears to be common to all proteins under conditions such that they do not pass directly into solution. The swelling caused by acids and alkalies is generally counteracted by the addition of neutral salt or by increasing the concentration of acid or alkali sufficiently.

While attempting to arrive at a rational explanation of the molecular mechanism of tanning, Procter was continually confronted by the necessity of first explaining the mechanism of swelling and to him belongs the credit of being the first to recognize the almost complete dependence of the science of leather chemistry upon the theory of swelling. In 1897 he started an investigation [7] of the swelling of gelatin in solutions of acids and salts which has culminated in the Procter-Wilson theory of swelling.

Procter's general method of experimentation was as follows: Sheets of thin, purified bone gelatin were cut into portions containing exactly 1 gram each of dry gelatin. A portion was put into each of a series of stoppered bottles containing 100 cubic centimeters of hydrochloric acid of definite concentration. After 48 hours, which was shown to be sufficient for the attainment of practical equilibrium, the remaining solution was drained off and titrated with standard alkali. The gelatin plates were quickly weighed and the volume of solution absorbed was calculated from the increase in weight of the plates. The swollen

[7] Action of Dilute Acids and Salt Solutions upon Gelatin. H. R. Procter. *Kolloidchem. Beihefte* (1911); *J. Am. Leather Chem. Assoc.* 6 (1911), 270.

portion expelled, due allowance being made for the increase in volume of solution due to saturating it with salt. The acid still unaccounted for was assumed to be combined with the gelatin base.

A further set of checks was obtained by dissolving the gelatin, dehydrated by treatment with salt, in warm water and titrating with standard alkali, using both methyl orange and phenolphthalein, the former indicating the free acid left in the jelly and the latter the total, including the acid combined with the gelatin base, which was obtained by difference.

Experimental values for the volume of solution absorbed by the gelatin, the free acid left in the external solution, the free acid in the jelly, and the acid combined with the gelatin base are shown in Table XI and in Figs. 42 and 43. These were taken from the table on page 317 of Procter's paper, The Equilibrium of Dilute Hydrochloric Acid and Gelatin.[8] In plotting the results, the concentration of gelatin chloride is taken as the difference between the concentrations of total chloride and free HCl in the jelly. The calculated values given along with the experimental ones will be discussed later in connection with the theory.

The Acid-Protein Equilibrium.

Procter recognized that gelatin combines with HCl forming a highly ionizable chloride and that the resulting equilibrium is a special case of the membrane equilibria described by Donnan. Instead of tracing the development of the theory of swelling from Procter's earliest work to its present status, it will simplify matters to present the theory from the deductive reasoning furnished later by Wilson and Wilson.[9] They set out to prove that the entire equilibria can be determined quantitatively from the orthodox laws of physical chemistry on the simple assumption that gelatin, or any protein, combines with hydrochloric acid to form a highly ionizable chloride. It seemed that success in this would furnish substantial proof of the correctness of the theory.

In order to make the reasoning general, let us consider the hypothetical protein G, which is a jelly insoluble in water, is completely permeable to water and all dissolved ionogens considered, is elastic and under all conditions under consideration follows Hooke's law, and com-

[8] *J. Chem. Soc.* 105 (1914), 313.

[9] Colloidal Phenomena and the Adsorption Formula. J. A. and W. H. Wilson. *J. Am. Chem. Soc.* 40 (1918), 886.

bines chemically with the hydrogen ion, but not the anion, of the acid HA according to the equation

$$[G] \times [H^+] = K[GH^+]. \qquad (1)$$

In other words, the compound GHA is completely ionized into GH^+ and A'.

Now take one millimole of G and immerse it in an aqueous solution of HA. The solution penetrates G, which thereupon combines with some of the hydrogen ions, removing them from solution, and consequently the solution within the jelly will have a greater concentration of A' than of H^+, while in the external solution $[H^+]$ is necessarily equal to $[A']$. The solution thus becomes separated into two phases, that within and that surrounding the jelly, and the ions of one phase must finally reach equilibrium with those of the other phase.

At equilibrium, in the external solution, let

$$x = [H^+] = [A']$$

and in the jelly phase let

$$y = [H^+]$$

and $$z = [GH^+]$$

whence $$[A'] = y + z.$$

It should be remembered that the brackets indicate concentration in moles per liter.

It is apparent from Donnan's line of reasoning, given earlier in the chapter, that the product $[H^+] \times [A']$ will have the same value in the external solution as in the jelly phase at equilibrium, or that

$$x^2 = y(y + z). \qquad (2)$$

As was pointed out above, it is evident from equation (2) that

$$2y + z > 2x$$

or $$2y + z = 2x + e \qquad (3)$$

where e is defined as the excess of concentration of diffusible ions of the jelly phase over that of the external solution. Where any two variables are known, all others can be calculated, for from equations (2) and (3) we get the following:

$$x = y + \sqrt{ey} = \sqrt{y^2 + yz} = (z^2 - e^2)/4e. \qquad (4)$$

$$y = (-z + \sqrt{z^2 + 4x^2})/2 = (2x + e - \sqrt{4ex + e^2})/2 = (z - e)^2/4e. \qquad (5)$$

$$z = (x^2 - y^2)/y = \sqrt{4ex + e^2} = e + 2\sqrt{ey}. \qquad (6)$$

$$e = (x - y)^2/y = z + 2y - 2\sqrt{y^2 + yz} = -2x + \sqrt{4x^2 + z^2}. \qquad (7)$$

Since [A′] is greater in the jelly than in the surrounding solution, the negative ions of the colloid compound will tend to diffuse outward into the external solution, but this they cannot do without dragging their protein cations with them. On the other hand, the cohesive forces of the elastic jelly will resist this outward pull, the quantitative measure of which is *e*, and according to Hooke's law

$$e = CV \tag{8}$$

where C is a constant corresponding to the bulk modulus of the protein and V is the increase in volume, in cubic centimeters, of 1 millimole of the protein.

Since we have taken 1 millimole of G,

$$[G] + [GH^+] = 1/(V + a)$$

or

$$[G] = 1/(V + a) - z \tag{9}$$

where *a* is the initial volume of 1 millimole of the protein.
From (1) and (9)

$$z = y/(V + a)(K + y) \tag{10}$$

and from (6) and (8)

$$z = CV + 2\sqrt{CVy}. \tag{11}$$

Now from (10) and (11)

$$(V + a)(K + y)(CV + 2\sqrt{CVy}) - y = 0 \tag{12}$$

where the only variables are V and *y*.

If the molecules or atoms of the protein are not themselves permeable to all ions considered, the quantity *a* should not be taken as the whole of the initial volume of the jelly, but only as the free space within the original, dry jelly through which ions can pass. For our hypothetical protein, then, we shall consider the limiting case where the value of *a* is zero. This assumption in the case of gelatin introduces errors less than the probable experimental error because of the relatively large values for V over the significant swelling range. Equation (12) thus reduces to

$$V(K + y)(CV + 2\sqrt{CVy}) - y = 0. \tag{13}$$

Knowing the values of the constants, K and C, we can plot the entire equilibrium as a function of any one variable. Procter and Wilson[10] obtained the value K = 0.00015 for the sample of gelatin used in their experiments by adding successive portions of standard HCl to a dilute solution of the gelatin and noting the corresponding rises in hydrogen-ion concentration. The difference between the concentration of hydrogen ion that would have been found upon adding the acid to pure water and that actually found by adding it to the same

[10] The Acid-Gelatin Equilibrium, *loc. cit.*

volume of gelatin solution was taken as the amount of acid combined with the gelatin, or as the value of $[GH^+]$ in equation (1). Substituting any two sets of determinations of $[GH^+]$ and $[H^+]$ in equation (1) and solving the resulting equations simultaneously, the value of K can be found.

C was obtained by substituting experimental values for V and *e* in

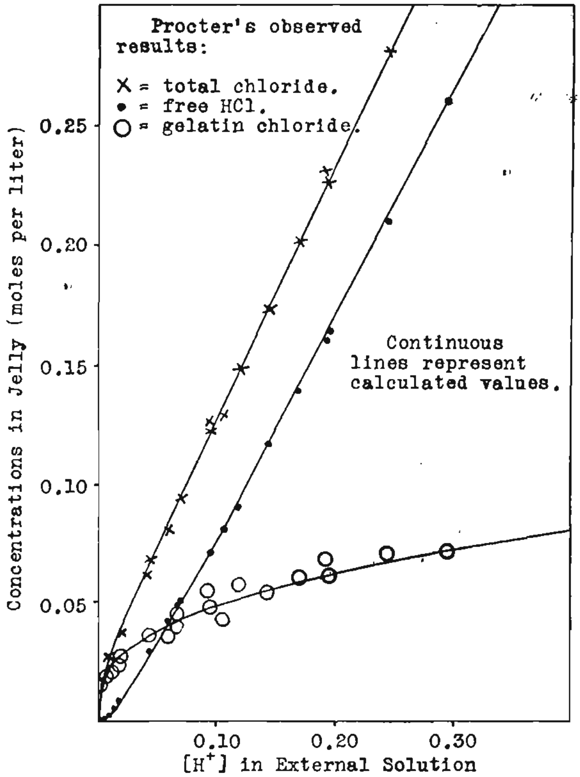


FIG. 42.—Observed and calculated values for the distribution of HCl in the system Gelatin-HCl-Water.

equation (8). It was found to vary with the temperature and with the quality of the gelatin, but had the value 0.0003 for the sample of gelatin used by Procter and at the temperature of his experiments, 18° C.

In order to compare calculated values for V with experimental determinations of the increase in volume of 1 gram of gelatin, it is necessary to know its equivalent weight. Procter originally regarded gelatin as a diacid base with a molecular weight of 839, but later work by Procter and Wilson showed that it should rather be regarded as acting as a monacid base, with an equivalent weight of 768, in acid solutions not sufficiently concentrated to cause decomposition. 768

grams of gelatin combine with a limiting value of 1 mole of hydrochloric acid and the combination resembles that of HCl with a weak monacid base. For this reason we may use the value 768 as the equivalent weight of gelatin. As for the molecular weight of gelatin, no convincing figures have yet been produced and it may be questioned whether

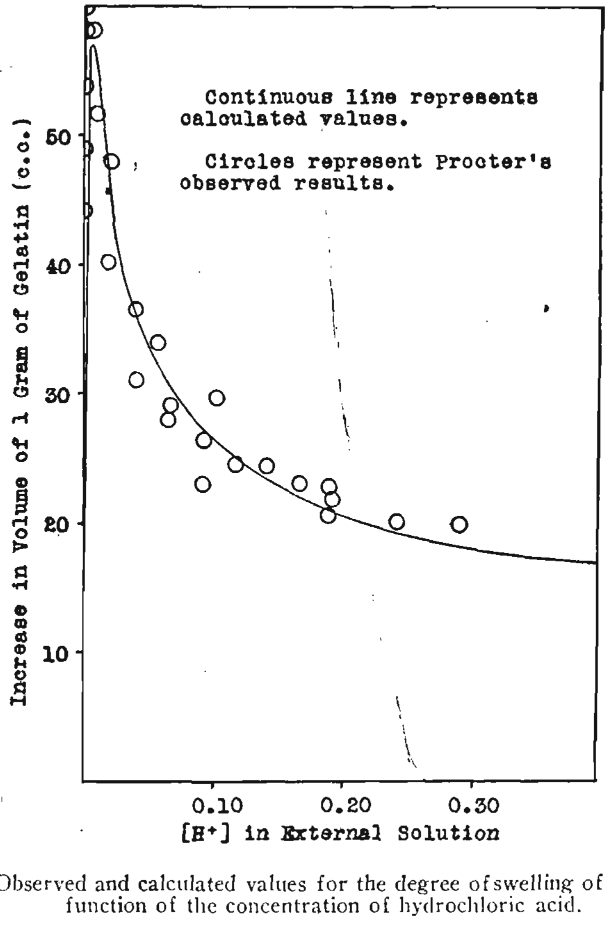


FIG. 43.—Observed and calculated values for the degree of swelling of gelatin as a function of the concentration of hydrochloric acid.

they would have any real value, if obtained. We look upon a plate of gelatin as a continuous network of chains of amino acids, there being no individual molecules, unless one wishes to look upon the plate of gelatin as one huge molecule.

From equation (13) and the values of the constants given above, Wilson and Wilson calculated all of the variables of the equilibrium for gelatin and hydrochloric acid over the range covered by Procter's

experiments. The important variables are shown in Table XI and in Figs. 42 and 43 along with Procter's actual determinations.

The agreement between calculated and observed values is absolute, within the limits of experimental error. For this reason Procter and Wilson regard their theory as proved, but, if further corroboration is desired, it can be found in the extensive researches of Loeb, some of which will be described later. *It is worthy of note that no other theory of swelling has yet passed the stage of qualitative speculation.*

TABLE XI.

	At Equilibrium							
			Cc. solution absorbed by 1 g. gelatin		[HCl] in jelly		[Total chloride] in jelly	
Initial [HCl]	[HCl] in soln.	V Calculated	Calculated	Observed	Calculated	Observed	Calculated	Observed
0.006	0.0011	33.3	43.4	44.1	0.0001	0.0005	0.012	0.014
0.008	0.0018	37.5	48.8	48.7	0.0002	0.0004	0.014	0.015
0.010	0.0025	41.7	54.3	59.9	0.0004	0.0004	0.016	0.015
0.010	0.0028	42.7	55.6	58.4	0.0004	0.0004	0.017	0.015
0.010	0.0032	43.2	56.2	53.7	0.0005	0.0005	0.019	0.017
0.015	0.0073	40.8	53.1	57.9	0.002	0.002	0.024	0.020
0.015	0.0077	40.2	52.3	52.2	0.002	0.002	0.025	0.022
0.015	0.0120	37.5	48.8	51.9	0.005	0.006	0.031	0.027
0.020	0.0122	37.3	48.6	51.7	0.005	0.006	0.031	0.027
0.025	0.0170	34.5	44.9	40.4	0.008	0.009	0.036	0.037
0.025	0.0172	34.3	44.7	48.1	0.008	0.009	0.036	0.031
0.050	0.0406	26.7	34.8	36.4	0.026	0.030	0.063	0.061
0.050	0.0420	26.4	34.4	31.1	0.027	0.030	0.065	0.068
.....	0.0576	24.0	31.2	34.0	0.041	0.043	0.082	0.079
0.075	0.0666	23.0	29.9	27.9	0.049	0.050	0.092	0.095
0.075	0.0680	22.8	29.7	29.1	0.050	0.053	0.094	0.092
0.100	0.0930	20.7	27.0	23.1	0.072	0.072	0.121	0.126
0.100	0.0944	20.5	26.7	26.4	0.073	0.072	0.122	0.121
.....	0.1052	19.8	25.8	29.8	0.083	0.085	0.134	0.128
0.125	0.1180	18.9	24.6	24.4	0.095	0.090	0.148	0.148
0.150	0.1434	17.9	23.3	24.0	0.118	0.118	0.174	0.173
0.150	0.1435	17.9	23.3	24.2	0.118	0.118	0.174	0.172
0.175	0.1685	17.1	22.3	23.5	0.141	0.138	0.200	0.200
0.200	0.1925	16.3	21.2	20.6	0.164	0.161	0.225	0.229
0.200	0.1940	16.2	21.1	22.7	0.166	0.165	0.227	0.225
0.200	0.1945	16.2	21.1	22.1	0.167	0.164	0.228	0.226
0.250	0.2450	15.1	19.7	20.2	0.213	0.210	0.279	0.281
0.300	0.2950	14.0	18.2	20.0	0.261	0.260	0.332	0.332

Other proteins which do not dissolve in cold water behave much like gelatin in respect to swelling, although they apparently have different values for the constants, K and C, as well as for equivalent weight. It is interesting to reason from the theory what differences in swelling would result from changes in the values of the constants. Since $V = e/C$, an increase in the value of C means a corresponding decrease in the degree of swelling. The effect of a change in the value of K, the hydrolysis constant of the protein, is shown in Fig. 44 for a fixed value of C. At $K = 0$, the point of maximum swelling occurs at

$x = 0$ and has the value $1/\sqrt{C}$. As K increases in value, the point of maximum swelling decreases in value and occurs at increasing values for x. At $K = \infty$, the point of maximum has the value zero and occurs at $x = \infty$

According to the theory, all monobasic acids should produce the same degree of swelling of gelatin for any fixed hydrogen-ion concen-

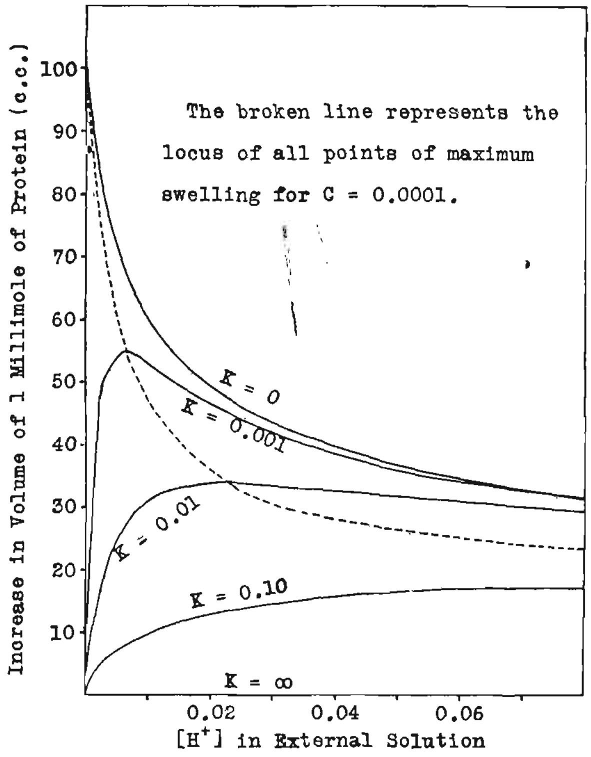


FIG. 44.—Family of swelling curves for proteins having the same bulk modulus, but different values for the hydrolysis constant.

tration, under constant conditions, provided the gelatin salts formed are ionized to the same extent. It was generally thought that different monobasic acids produce different degrees of swelling, following the order of the well-known Hofmeister series of the ions, until Loeb pointed out that the earlier investigators, through failure to measure the hydrogen-ion concentration, had fallen into the error of attributing to the several acids effects caused merely by differences in hydrogen-ion concentration. He found, at a fixed value for x, that practically the same degree of swelling is produced by all monobasic acids, as well as

such acids as phosphoric and oxalic at concentrations at which they act as monobasic.

The calculation of the degree of swelling of proteins in solutions of polybasic acids is not quite so simple as for monobasic acids. Suppose that G were to combine with the hydrogen ion but not the anion of the polybasic acid H_aA. Letting x represent the concentration of the polyvalent anion in the external solution at equilibrium, z the concentration of the anion of the gelatin salt, and $y + z$ the total concentration of anion in the jelly, it is evident from the reasoning given above that

$$x^{a+1} = y^a(y + z)$$

and, by inspection of this equation, we see that

$$(a + 1)x < (a + 1)y + z$$

or that

$$(a + 1)x + e = (a + 1)y + z.$$

The total concentration of diffusible ions is greater in the jelly than in the external solution by the amount e and swelling in degree directly proportional to e will result. It can readily be seen that as x increases from zero, without limit, e and the degree of swelling increase to a maximum and then decrease, approaching zero, for z has a limiting value since it cannot exceed the total concentration of gelatin. At $x = 0$, $y = 0$, and $e = 0$. As x increases without limit our equations approach the limiting relations

$$x^{a+1} = y^{a+1}$$

and

$$(a + 1)x + e = (a + 1)y$$

from which it is evident that $x = y$ and $e = 0$.

The extent of swelling by polybasic acids which combine as such with the protein will be considerably less than that caused by monobasic acids, as Loeb has shown, because fewer anions will be associated with equivalent weights of the protein. For example, for equivalent weights of gelatin sulfate and gelatin chloride, there would be only half as many sulfate ions as chloride ions. For very small values of x, we should therefore expect sulfuric acid to produce only half as much swelling as hydrochloric acid at the same hydrogen-ion concentration and this is actually the case.

Repression of Swelling by Salts.

The theory accounts quantitatively for the action of neutral salts in repressing the swelling of proteins by acid. In the system described above in which the protein G was immersed in a solution of HA, consider the addition of the mono-monovalent salt MN, neither of whose ions combine with G. At equilibrium, let the concentration of M^+ be represented by u in the external solution and by v in the jelly. It is evident from the general equation of products that the product

$$([H^+] + [M^+]) \times ([A'] + [N'])$$

will have the same value in both phases, or that

$$(x + u)^2 = (y + v)(y + v + z),$$

from which

$$e = 2(y + v) + z - 2(x + u).$$

Solving the two preceding equations simultaneously, we get

$$e = -2(x + u) + \sqrt{4(x + u)^2 + z^2}.$$

Now, if the value of $x + u$ increases while z remains constant, the value of e, and consequently the swelling, will decrease. The addition of MN to the system increases u and hence must cause a decrease in the degree of swelling, since it increases z only by causing a diminution of the volume of the jelly.

It is important to recognize that the repression of swelling by salts does not depend upon any repression of ionization of the protein salt. The salt acts so as to lower the value of e, which is the measure of the force producing swelling. In some cases, the ionization may be repressed to some extent and this would assist in repressing the swelling, but in the case of gelatin chloride, the swelling is markedly reduced long before there is any repression of ionization of gelatin chloride measurable by means of calomel electrodes.

The Alkali-Protein Equilibrium.

Proteins are amphoteric substances, reacting both as weak acids and as weak bases. In this respect, they retain the properties of the amino acids from which they are formed. Hydrated aminoacetic acid is capable of assuming either a positive or negative charge, or both, by ionizing as acid or base, or both, thus:

$$H^+ + 'OOC.CH_2.NH_2.HOH = HOOC.CH_2.NH_2.HOH = HOOC.CH_2.NH_2.H^+ + OH'.$$

The ionization constant of a protein as an acid may be represented as follows:

$$[H^+] \times [G'] = K_a[GH].$$

But $\quad [H^+] \times [OH'] = K_w$ or $[H^+] = K_w/[OH']$

from which $\quad [GH] \times [OH'] = k[G']$, where $k = K_w/K_a$.

But this is essentially the same as equation (1) except for the fact that $[H^+]$ is replaced by $[OH']$. It is thus apparent that proteins will behave in solutions of increasing concentration of alkali much as they do in solutions of acids so long as they undergo no chemical changes other than that of salt formation. Actually gelatin swells in alkaline solution to a maximum at a concentration of about 0.004 mole of hydroxide ion per liter, above which the swelling diminishes.

In acid solution maximum swelling occurs at a concentration of 0.004 mole of hydrogen ion per liter.

The effect of valency is similar in both acid and alkaline solutions. Loeb found that the diacid bases calcium hydroxide and barium hydroxide give points of maximum swelling for gelatin only half as great as the monacid bases. For a given pH value, the amount of swelling is determined by the valency of the ions of opposite sign to that of the protein ions rather than by the specific nature of the ions themselves.

TABLE XII.

ISOELECTRIC POINTS OF SEVERAL PROTEINS IN TERMS OF — LOG [H^+] OR pH VALUE.

	— Log [H^+] or pH value	Reference
Casein (cow)	4.6	1
	4.7	2
	4.7	3
Gelatin	4.6	4
	4.7	5
Serum albumin	4.7	6
Serum globulin	5.4	2
Egg albumen (hen)	4.8	7
Denatured serum albumin	5.4	6
Oxyhemoglobin	6.7	9
Carbon monoxide hemoglobin	6.8	10
Reduced hemoglobin	6.8	10
Stroma globulins of blood corpuscles	5.0	8, 9
Red blood cells	4.6	11
Yeast extract proteins (globulin)	4.6	14
Gliadin	9.2	2
Edestin	5.6	15
Tuberin (potato)	approx. 4.0	12
Carrot protein	" 4.0	12
Tomato protein	" 5.0	12
Nucleic acid	" 2.0	13

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In alkaline solution the protein ion is negatively charged, while it is positively charged in acid solution. In a solution, originally alkaline, in which the hydrogen-ion concentration is gradually increased, there must be some point at which the protein becomes electrically neutral; that is, where it has an equivalent number of positive and negative charges. The hydrogen-ion concentration at which this occurs has

been called by Hardy[11] the isoelectric point of the protein. The isoelectric point of gelatin was found by Michaelis and Grineff[12] to lie at a pH value of 4.7 and this value has been repeatedly confirmed by Loeb and others.

Thomas and Kelly[13] determined the isoelectric point of collagen, or rather hide powder, by means of acid and basic dyes. Portions of hide powder were first wet with solutions of different pH values, then with solutions of basic fuchsin or Martius yellow, and finally washed with solutions having the same pH values as were used to wet the portions initially. The fuchsin left the hide powder deeply stained only at pH values greater than 5 and the Martius yellow only at values below 5, indicating pH = 5 as the isoelectric point of collagen.

Porter[14] observed that a point of minimum swelling of hide powder occurs at a pH value of 4.8, indicating this as its isoelectric point. Porter also found points of maximum swelling of hide powder at pH values of 2.4 in acid solution and about 12.3 in alkaline solution.

Thomas and Kelly compiled a list of isoelectric points of different proteins, taken from the literature, and these are reproduced in Table XII in terms of pH value.

Two Forms of Collagen and Gelatin.

Quantitative experiments upon alkaline swelling are rendered difficult by the tendency for the gelatin to pass into solution, which is very much more marked than for acid swollen gelatin. That gelatin and some other proteins undergo a change of form in alkaline solutions is apparent from recent experimental data. Lloyd[15] observed a rather significant change occurring in gelatin dissolved in alkaline solution. A comparison between gelatin dissolved in acid solution and gelatin dissolved in alkaline solution was made as follows.

Two grams of gelatin were put into a flask containing 200 cubic centimeters of tenth-molar hydrochloric acid. After 6 days at 20° C., the gelatin was completely dissolved and 20 cubic centimeters of molar sodium hydroxide were added to the solution, which was then tested and found to be neutral to litmus. 220 cubic centimeters of saturated ammonium sulfate solution were then added and a white, flocculent precipitate formed, which was filtered off. The filtrate was tested and found to be free from protein. The precipitate was insoluble in cold water and was washed several times. It was dissolved in 2 cubic centimeters of hot water and set to a jelly upon cooling. A control experiment made by dissolving 2 grams of gelatin in 220 cubic centimeters of water with 1.12 grams of sodium chloride behaved in a similar manner.

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[12] *Biochem. Z.* 41 (1912), 373.
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[14] Swelling of Hide Powder. E. C. Porter. *J. Soc. Leather Trades Chem.* 5 (1921), 259, and 6 (1922), 83.
[15] On the Swelling of Gelatin in Hydrochloric Acid and Caustic Soda. D. J. Lloyd. *Biochem. J.* 14 (1920), 147.

For comparison, 2 grams of gelatin were put into a flask containing 200 cubic centimeters of tenth-molar sodium hydroxide. The gelatin was completely dissolved after 2 days at 20° C. 20 cubic centimeters of molar hydrochloric acid were then added to the solution, after which it reacted neutral to litmus. 220 cubic centimeters of saturated ammonium sulfate solution were added and a white, flocculent precipitate formed, which was filtered off. The filtrate, as in the

TABLE XIII.

SWELLING OF GELATIN IN PHOSPHATE BUFFER SOLUTION DURING 4 DAYS AT 7° C.

pH value of buffer solution at 20° C. Initial	Final	Increase in wt. of 1 g. dry gelatin Grams
2.90	2.92	13.20
3.50	3.50	9.49
3.96	4.01	7.72
4.14	4.17	6.91
4.47	4.59	6.68
4.78	4.86	6.20
5.08	5.12	7.02
5.29	5.38	7.13
5.57	5.61	7.22
5.78	5.80	7.56
6.04	6.08	7.80
6.29	6.29	7.83
6.48	6.49	8.02
6.69	6.70	8.29
6.96	6.94	8.31
7.08	7.10	8.25
7.41	7.37	8.03
7.68	7.62	7.62
7.97	7.89	8.39
8.42	8.36	8.59
8.56	8.48	8.60
9.03	8.96	8.78
9.57	9.51	8.91
10.00	9.96	8.98
10.47	10.41	9.24
11.06	10.98	9.55
11.52	11.48	9.95
12.00	11.95	10.73

previous experiment, was found to be free from protein. But the precipitate dissolved completely and rapidly in a small volume of cold water and would not set to a jelly even when the volume was reduced to 2 cubic centimeters.

Lloyd suggested that gelatin changes from a keto-form to an enol-form in alkaline solution. The gelatin recovered from acid solution and which had the power of setting to a jelly would thus be regarded as the keto-form of gelatin, while that recovered from alkaline solution and which had lost the power of setting to a jelly would be looked upon as the enol-form of gelatin. Miss Lloyd regarded the change in alkaline solution as irreversible, but her experiments do not

show this. Mr. Kern, in the author's laboratory, added hydrochloric acid to gelatin dissolved in a hot solution of sodium hydroxide until the pH value, as determined by the hydrogen electrode, was reduced to 4.7 and then allowed the solution to cool, whereupon it set to a firm jelly, indicating that the change is reversible. Miss Lloyd's ex-

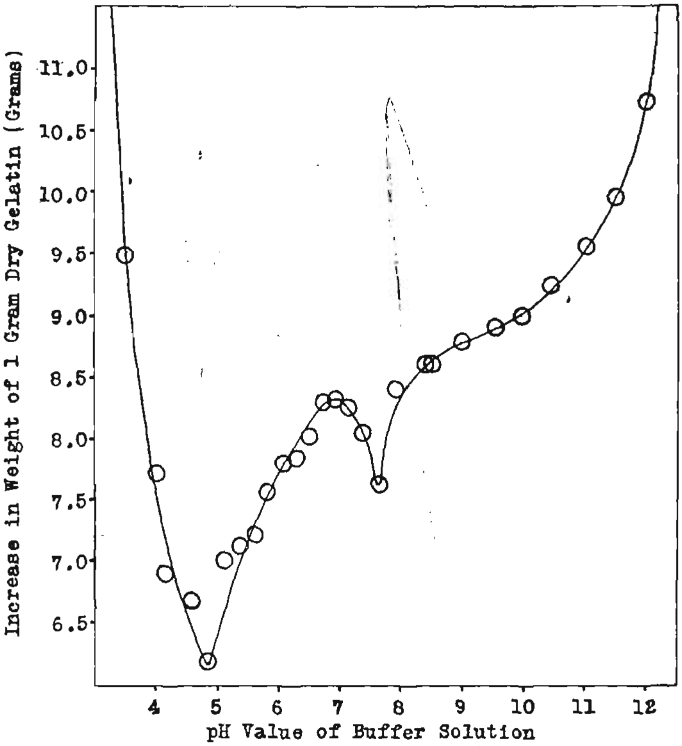


FIG. 45.—Showing the two points of minimum swelling of gelatin.

periment showed merely that it is not readily reversed by the addition only of the quantity of hydrochloric acid equivalent to that of the sodium hydroxide originally employed.

In studying the degree of plumping of calf skin as a function of pH value, Wilson and Gallun found two points of minimum, one at 5.1 and the other at 7.6. This work will be described in Chapter 9. Wilson and Kern [16] followed this with a series of experiments upon the swelling of gelatin in buffer solutions and also found two points of minimum, one at 4.7 and the other at 7.7. A description of their work follows.

[16] The Two Forms of Gelatin and Their Isoelectric Points. J. A. Wilson and E. J. Kern. *J. Am. Chem. Soc.* 44 (1922), 2633.

A series of buffer solutions was prepared, each member of which had a final concentration of tenth-molar phosphoric acid plus the amount of sodium hydroxide required to give the desired pH value as determined by the hydrogen electrode at 20° C. The pH values ranged from 3 to 12. 200 cubic centimeters of each solution were put into a stoppered bottle and kept in a thermostat refrigerator at 7° C. After the temperature of each solution had reached 7°, a small strip of high grade gelatin of known weight was put into it. All strips were taken as nearly alike as possible and were kept in the solutions at 7° for 4 days, after which each strip was quickly blotted off and weighed. The results were carefully rechecked. In Table XIII are given the gain in weight per gram of dry gelatin and the initial and final pH values of the buffer solutions. Fig. 45 represents the degree of swelling as a function of the pH value.

Wilson and Kern suggested that the two points of minimum represent the isoelectric points of the two forms of gelatin described by Lloyd and this view appears to be substantiated by other data available in the literature.

Experiments upon the mutarotation of gelatin led Smith [17] to suggest that gelatin exists in two forms: a sol form, having a specific rotation of $[\alpha]_D = -141$ and being stable at temperatures above 35° C., and a gel form, with a specific rotation of $[\alpha]_D = -313$ and stable under 15°, a condition of equilibrium existing between the two forms at intermediate temperatures. The gel form is characterized by its power to set to a jelly, which is lacking in the sol form. Smith calculated that a concentration of from 0.6 to 1.0 gram of the gel form per 100 cubic centimeters is required to produce gelation. As the temperature is increased above 15°, the total concentration of gelatin required to produce gelation is increased because of the decreasing proportion of the gel form, which does not exist at all above 35° C. Gelatin is the only protein known to show mutarotation, but it gradually loses this property along with its jellying power, when its solutions are kept at temperatures above 70° C.

Davis and Oakes [18] measured the viscosities of a series of solutions of gelatin at 40° C. at different pH values. Their results are shown in Fig. 46. A point of minimum occurs at 8, but none at 4.7, the isoelectric point of gelatin as determined by Loeb. They commented upon this as follows: "There may be considerable difficulty in reconciling this minimum viscosity at pH about 8 with the isoelectric point at pH 4.7." But Davis and Oakes really measured the point of minimum viscosity of the sol form, since their determinations were made at 40° C., whereas Loeb determined the isoelectric point of the gel form.

Another case of the apparent disappearance of an isoelectric point when working at a temperature of 40° C. is to be found in the work of Wilson and Daub,[19] who experimented upon the bating of calf skin at

[17] Mutarotation of Gelatin and Its Significance in Gelation. C. R. Smith. *J. Am. Chem. Soc.* 41 (1919), 135.

[18] Further Studies of the Physical Characteristics of Gelatin Solutions. C. E. Davis and E. T. Oakes. *J. Am. Chem. Soc.* 44 (1922), 464.

[19] A Critical Study of Bating. J. A. Wilson and G. Daub. *J. Ind. Eng. Chem.* 13 (1921), 1137.

40° at different pH values. They observed that a point of minimum plumping occurred in the region of pH = 8, but not at pH = 5, the isoelectric point of collagen found by Thomas and Kelly and by Porter. But Wilson and Gallun observed points of minimum plumping of calf skin at both 5 and 8, when working at low temperatures. The recent work of Sheppard, Sweet and Benedict [20] adds further evidence of the existence of critical pH values at both 5 and 8. They obtained a

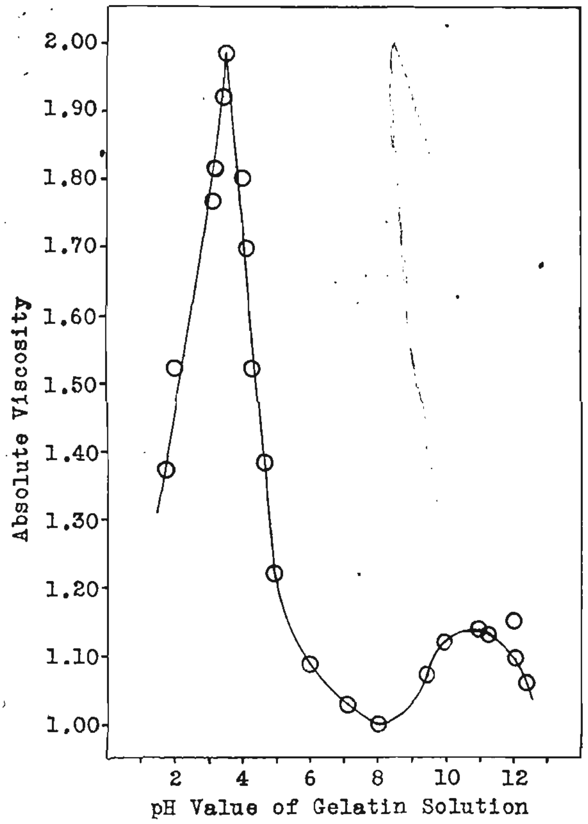


FIG. 46.—Variation of viscosity of 1-per cent solution of gelatin at 40° C. with change of pH value.

curve for the rigidity of gelatin jelly as a function of pH value exhibiting a shoulder at 5 and a flattish maximum between 7 and 9.

Apparently the change in gelatin from the gel form to what has been called the sol form takes place both with rise of temperature and with rise of pH value. Since the experiments of Wilson and Kern were performed at 7° C., they were dealing with the gel form of gelatin

[20] Elasticity of Purified Gelatin Jellies as a Function of Hydrogen-Ion Concentration. S. E. Sheppard, S. S. Sweet and A. J. Benedict. *J. Am. Chem. Soc.* 44 (1922), 1857.

in acid solution and actually observed a point of minimum at pH = 4.7, the isoelectric point of the gel form. The appearance of a second point of minimum swelling at pH = 7.7 seems to indicate that between 4.7 and 7.7 the gelatin passes from the gel to the sol form and that the second point of minimum occurs at the isoelectric point of the sol form. It was only by working at temperatures as low as 7° that they were able to prevent the gelatin from passing into solution at the higher pH values.

While objection may be raised to the terms gel and sol form as applied to the two forms of gelatin and of collagen, they will serve as well as any until more is known of the transition. Lloyd's suggestion that the change is a keto-enol tautomerism is still speculative.

Parker Higley,[21] at the University of Wisconsin, has recently investigated the absorption spectra of gelatin dispersions of different pH value and plotted a series of curves, at several densities, for the wave *length of maximum absorption in the ultra violet as a function of pH* value. The curves all show two points of minimum, one at pH = 4.68 and the other at 7.66, coinciding with the points of minimum swelling of gelatin. That the two points of minimum have a real existence is thus strikingly confirmed from an unexpected source.

The effect upon vegetable tanning of the change of one form of collagen to the other will be discussed in Chapter 13.

Electrical Potential Difference between Protein Jelly and Aqueous Solution.

It is apparent from the discussion of Donnan's theory of membrane equilibria that the unequal distribution of ions between a jelly and its surrounding solution must give rise to an electrical difference of potential between these two phases whose measure is $(RT/F).\log(x/y)$, where x is the hydrogen-ion concentration of the external solution and y that of the solution within the jelly and this value holds true regardless of the valence or number of ions in the system. The potential difference can therefore be calculated from the determinations of pH value in the jelly and in the external solution. Changing from natural to common logarithms and substituting the numerical value for RT/F at 20° C., we get.

$$\text{P.D.} = 58\log(x/y) = 58(\log x - \log y) \text{ millivolts.}$$

But $-\log y =$ pH value of the jelly and $+\log x = -$ pH value of the solution. Hence, at 20° C,

$$\text{P.D.} = 58(\text{pH of jelly minus pH of solution}) \text{ millivolts.}$$

Loeb[22] devised a very ingenious method for determining this potential difference directly by means of a pair of calomel cells of equal value

[21] Advance note.
[22] Cf. Proteins and the Theory of Colloidal Behavior, p. 154.

and a Compton electrometer. A diagram of his apparatus is shown in Fig. 47. The potential difference measured is that of the cell

calomel electrode	saturated KCl	external solution	solid jelly	saturated KCl	calomel electrode

Everything else being symmetrical, the potential difference measured is that between the jelly and the external solution with which it is supposed to be at equilibrium.

In a typical experiment,[23] 1 gram of purified gelatin, powdered to a grain size between 30 and 60 mesh, was put into each of a series of solutions of different concentrations of hydrochloric acid or sodium

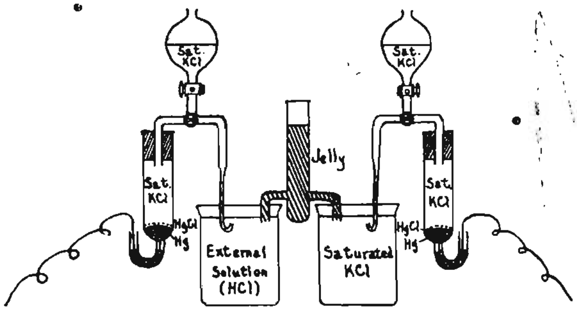


FIG. 47.—Loeb's apparatus for measuring the potential difference between gelatin jelly and the surrounding solution.

hydroxide. The volume of each solution was 350 cubic centimeters and the temperature 20° C. After 4 hours the volume occupied by each portion of gelatin was measured, the solution filtered off, and the gelatin melted so that the pH values of both jelly and solution could be determined by means of the hydrogen electrode. The gelatin was then allowed to set to a jelly in the receptacle illustrated in Fig. 47 and the potential difference between the jelly and external solution was then measured with a Compton electrometer. The results of such a series are shown in Table XIV along with calculations of the potential differences made from the pH determinations. The calculated and observed results are at least of the same sign and order of magnitude, which is a good agreement considering the nature of the experiments and the dilutions of the solutions. It will be shown later that the method is capable of very much better agreement where the complications involved in melting and resetting of the jelly are avoided, as in the measurement of potential difference between a solution of gelatin and a protein-free solution with which it is in equilibrium and from which it is separated by a semi-permeable membrane, especially where the solutions have greater conductivities.

[23] The Origin of the Electrical Charges of Colloidal Particles and of Living Tissues. Jacques Loeb. *J. General Physiol.* 4 (1922), 351.

According to the theory, the concentration of free acid in an acid-swollen jelly should be less than that in the external solution and, likewise, the concentration of free alkali in an alkali-swollen jelly should be less than that in the external solution with which it is in equilibrium.

TABLE XIV.

SUSPENSIONS OF POWDERED GELATIN.

After 4 hours at 20° C.

Initial normality of solution	Vol. of gelatin (mm.)	pH value of Absorbed solution (a)	pH value of External solution (b)	(a) minus (b)	P.D. millivolts Calculated	P.D. millivolts Observed
0.0010N HCl	28	4.44	3.35	+ 1.09	+ 63.0	+ 56.0
0.0005N HCl	20	4.56	3.55	+ 1.01	+ 58.6	+ 55.5
0.0002N HCl	18	4.79	3.92	+ 0.87	+ 51.0	+ 36.5
0.0001N HCl	16	4.85	4.24	+ 0.61	+ 36.0	+ 15.0
Water	17	4.89	4.97	— 0.08	— 4.5	— 17.5
0.0001N NaOH	18	4.98	5.96	— 0.98	— 57.0	— 59.0
0.0002N NaOH	28	5.06	6.24	— 1.18	— 68.0	— 61.0
0.0005N NaOH	37	5.50	6.46	— 0.96	— 56.0	— 70.0
0.0010N NaOH	40	6.74	7.30	— 0.56	— 33.0	— 66.0
0.0020N NaOH	47	9.54	10.56	— 1.02	— 59.0	— 46.0
0.0040N NaOH	48	10.15	11.08	— 0.93	— 48.0	— 36.0

This is verified by the figures in Table XIV, which show, for pH values of the external solution less than 4.7, that the hydrogen-ion concentration is greater in the solution than in the jelly, while for pH values of the external solution greater than 4.7, the hydrogen-ion concentration is less or the hydroxide-ion concentration greater in the solution than in the jelly.

Rhythmic Swelling of Protein Jellies.

Sheppard and Elliott [24] made a study of the causes of the reticulation of the surfaces of photographic negatives that has a bearing upon a similar kind of trouble sometimes occurring in the vegetable tanning of skins. During the fixing or washing of a negative, the wet gelatin layer sometimes becomes more or less finely wrinkled or corrugated, the network of puckers forming a pattern extending either over the whole of the negative or only over part of it. They found that this reticulation can be produced by the combined action of a swelling agent and a tanning agent.

Fig. 48 represents a print from a negative treated to produce reticulation by Mr. Daub in the author's laboratories. The plate was flashed, developed, fixed with sodium thiosulfate, washed, and then immersed in a solution of wattle bark extract containing 5 grams of tannin and 0.2 mole of acetic acid per liter; the temperature was kept at

[24] The Reticulation of Gelatine. S. E. Sheppard and F. A. Elliott. *J. Ind. Eng. Chem.* 10 (1918), 727.

28° C. After several minutes the gelatin surface began to pucker at isolated points and this action gradually spread over the entire surface, producing series of ridges of swollen gelatin with valleys of hardened and contracted gelatin in between. Following this action, the silver particles migrated from the hardening portions into the swelling ridges, giving the negative the mosaic-like appearance shown in the print. Often the puckering became well pronounced before the

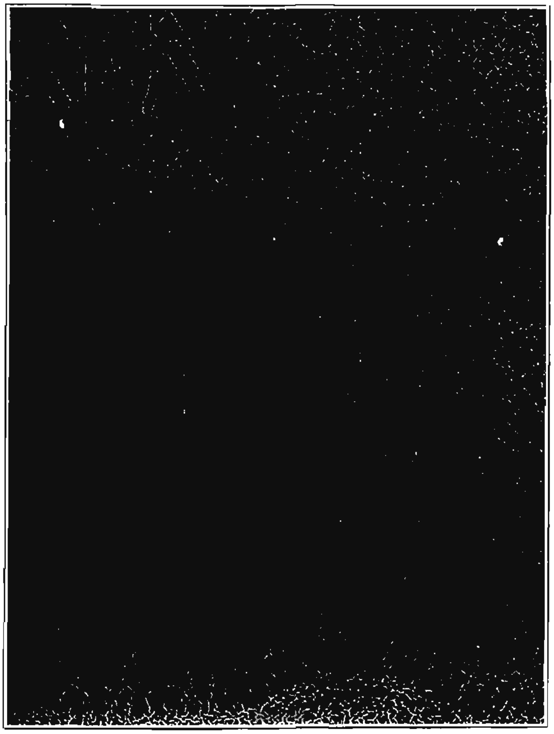


Fig. 48.—Reticulation Produced on Photographic Negative.

migration of silver particles was noticeable. Sheppard and Elliott liken the effect to the production of Liesegang rings.

The acid tends to cause a swelling of the gelatin while the tannin tends to cause a hardening and contracting action. But the acid diffuses relatively very rapidly whereas the diffusion of the tannin is greatly retarded both by its high molecular weight and by its tendency to combine with the gelatin, forming a compound less permeable and having a much lower power of swelling than the original gelatin. The action becomes greatly accelerated as the temperature is raised towards the melting point of the gelatin jelly. When the action is prolonged

at higher temperatures, provided the jelly does not dissolve, a second and much coarser series of puckers begins to form, tending to mask the finer pattern. In the coarser pattern, the peaks of the ridges may be from one to several millimeters apart.

The reticulation of the surface of skin in tanning is a very serious matter as the pattern formed is permanent and materially reduces the selling value of the leather. The pattern formed on skins is usually of the coarser variety and would hardly pass as an artistic sample of embossing, which the photographic negative might do, because of the fineness of the pattern and distribution of silver particles. The reticulation of skin may attend the injudicious use of acid in attempting to plump the leather during tanning, or it may occur where acid-producing ferments get the upper hand in a yard where fresh liquors are normally used. The corrective is to prevent the swelling action, either by neutralization of the acid or by the addition of salt.

Structure of Gelatin Solutions and Jellies.

Procter's [25] investigations of the behavior of gelatin jellies led him to regard them as having a structure consisting of a network of molecules cohering to each other, but leaving interstices large enough to permit the passage of water and simple molecules and ions. The long chains of amino acids making up the protein molecules are peculiarly fitted to produce such a structure through combination of the acid and basic terminals of these chains. A hot solution of gelatin may be looked upon as a true solution consisting of individual gelatin molecules, or at least of comparatively small polymerized groups, but the molecules orientate themselves, as the solution cools, so as to leave a minimum of free energy, the most active acid groups tending to unite with the most active basic groups until a continuous network is formed throughout the system. A block of jelly might thus be looked upon as an enormous, single molecule. Such a view is not radical in the light of modern theories of crystal structure.

According to the Procter-Wilson theory of swelling, when a block of gelatin jelly is immersed in a solution of hydrochloric acid, the solution passes into the jelly, filling up the interstices. Of the ionized gelatin chloride, which then forms, the chloride ions remain in the solution in the interstices while their corresponding gelatin cations form part of the network and are not in solution in the same sense as the anions. In tending to diffuse into the outer solution, the anions exert a pull upon the cations forming part of the network, causing an increase in volume of the jelly proportional to the pull exerted, so long as the elastic limit is not exceeded. That gelatin jellies are truly elastic and follow Hooke's law may be taken as proved chemically by the agreement between calculated and observed results shown in Table XI. More recently Sheppard and Sweet [26] proved by measure-

[25] The Structure of Organic Jellies. H. R. Procter. *Proc. Seventh International Congress of Applied Chemistry*, London, 1909.

[26] The Elastic Properties of Gelatin Jellies. S. E. Sheppard and S. S. Sweet. *J. Am. Chem. Soc.* 43 (1921), 539.

ments of rigidity that gelatin jellies follow Hooke's law nearly up to the breaking point.

Loeb's work on the viscosity of gelatin solutions, to be discussed presently, indicates that the initial step in gelation is the combination of individual molecules to form large aggregates, possibly in a manner similar to the growth of crystals. Bogue[27] pictures this process as the formation of catenary threads by the union of the individual molecules end to end. The manner in which fibrous curds of soap are formed led McBain[28] to a similar view regarding the structure of soap jellies and solutions. He attributes the elasticity of gels to the formation of an exceedingly fine filamentous structure. Innumerable molecules placed lengthwise and held together by forces of residual valence are assumed to make up these fine threads, which may be microns or millimeters in length.

Considering the nature and variety of the amino acids composing the gelatin molecule, as shown in Table I of Chapter 3, we should hardly expect the polymerization of gelatin to take place along a single line, but in every direction and probably with cross chains growing to support chains increasing in length in other directions. The increasing viscosity of gelatin solutions with time, upon cooling, would thus be attributed to the increasing size of the particles; the formation of a rigid jelly to the final union of the large particles, forming a structure continuous throughout the entire system.

There is an abundance of evidence to support Procter's view of the structure of jellies and Loeb's view that gelatin solutions, after standing for a time at temperatures below 35° C., always contain particles of jelly consisting of aggregates of gelatin molecules. A number of supporting lines of evidence are given in a review of the literature by Thompson.[29]

Graham showed long ago that the velocity with which crystalloids diffuse through gelatin jellies is only very little less than the velocity through pure water. This slight reduction in velocity is in no way comparable with the apparently great physical difference in state between the jelly and water. Although the viscosity of a gelatin jelly is too great to be measured by the methods usually applied to liquids, simple molecules move through it as though in a medium of viscosity nearly that of water. The network theory explains this by assuming that the diffusing substance actually is moving through the pure water or aqueous solution in the interstices of the network. Any slight diminution in velocity can be accounted for by the small portion of any cross section of the jelly occupied by the gelatin network. The same holds true for gelatin solutions, the diffusing substance being able to pass through the particles of jelly in suspension almost as rapidly as through the solution surrounding the particles.

[27] Properties and Constitution of Glues and Gelatines. R. H. Bogue. *Chem. Met. Eng.* 23 (1920), 61.

[28] Colloid Chemistry of Soap. J. W. McBain. *Brit. Assoc. Advancement Sci. Third Report on Colloid Chemistry* (1920), 2.

[29] Structure of Gelatin Solutions. F. C. Thompson. *J. Soc. Leather Trades Chem.* 3 (1919), 209.

Thompson shows from the work of Dumanski[30] that the conductivity of a solution of potassium chloride in gelatin jelly is no less than in pure water when a correction is made for the small volume actually occupied by the gelatin network, whereas, if the apparent viscosity had any effect, the conductivity should be reduced by the gelatin to a minute fraction of its value in pure water.

The vapor pressure of even a 20-per cent gelatin jelly is practically the same as that of water, indicating the presence of pure water in accordance with the network theory.

By placing a strain upon gelatin jelly in one direction, double refraction is produced, a property always associated with a definite structure and with anisotropy. Even dilute solutions of gelatin show double refraction on compression or when passed between two cylinders rotating in opposite directions. With increasing strain, the effect is increased up to a point corresponding to an elastic limit. This indication of structure even in gelatin solutions corroborates the views of Loeb and of Bogue.

The fact that the viscosity of gelatin solutions is lowered by simply agitating the solution is another piece of evidence in favor of the existence of a structure in gelatin solutions and still further evidence is furnished by Loeb's work on the viscosity of gelatin solutions and Bogue's measurements of plasticity, to be described later.

Relation of the Osmotic Pressure and Viscosity of Gelatin Solutions to the Swelling of Gelatin Jellies.

In an extensive series of experiments, Loeb has shown that the variations in osmotic pressure and viscosity of gelatin solutions with change of pH value or of concentration of salt, parallel the corresponding variations in the degree of swelling of gelatin jellies, which is what would be expected on the basis of the theory of protein-salt formation described above. This parallelism is shown by the curves in Figs. 49 to 54.

In each determination[31] of the two series of experiments performed to get the curves shown in Fig. 49, 1 gram of powdered gelatin was put for 1 hour at 20° C. into 100 cubic centimeters of acid solution of definite strength. The volume of the gelatin was measured, after settling, in a graduated cylinder and the pH value of the jelly was determined after melting. The volume is plotted against the pH value of the jelly and not that of the external solution, which was always lower, as explained in the discussion of the theory of swelling.

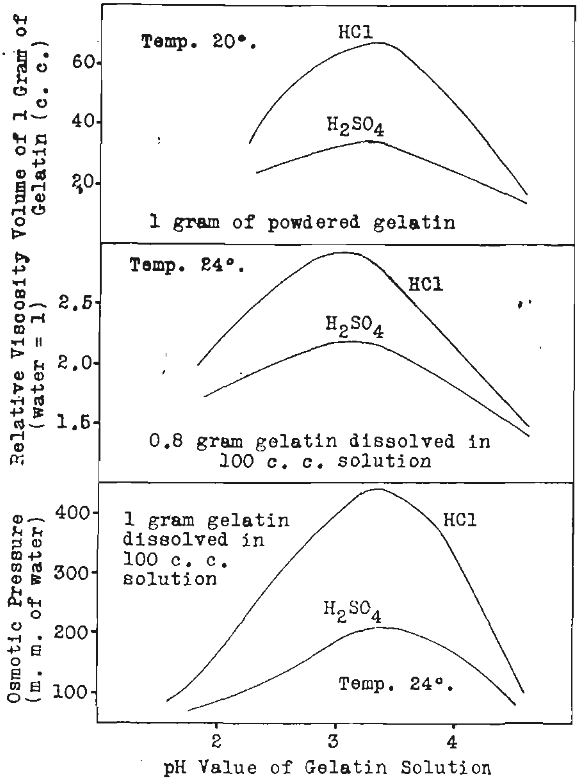
The curves in Fig. 50 were obtained by rapidly heating to 45° C. solutions of 0.8-per cent gelatin containing different amounts of acid, maintaining this temperature for 1 minute, cooling rapidly to 24°, and immediately determining the viscosity at 24°. The viscosity is plotted against the pH value of the gelatin solution.[32]

[30] *Z. physik. Chem.* 50 (1907), 553.

[31] Ion Series and the Physical Chemistry of the Proteins; II. Jacques Loeb. *J. General Physiol.* 3 (1920), 247.

[32] Ion Series and the Physical Properties of Proteins; I. Jacques Loeb. *J. General Physiol.* 3 (1920), 85.

In the experiments whose results are shown in Fig. 51, collodion bags, cast in the form of Erlenmeyer flasks having a volume of 50 cubic centimeters, were filled with 1-per cent gelatin solutions containing different amounts of acid. Each bag was closed with a rubber stopper fitted with a glass tube serving as a manometer and put into



Variables as Functions of pH Value.

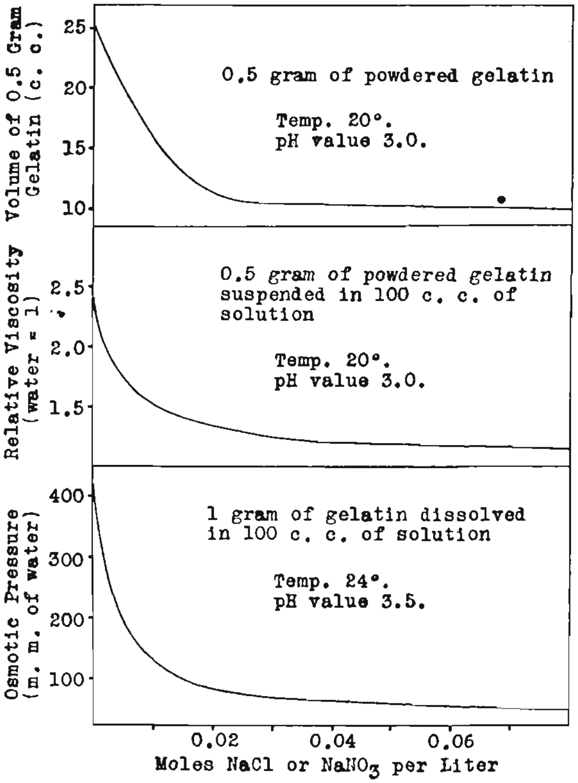
FIG. 49.—Volume of powdered gelatin.
FIG. 50.—Viscosity of gelatin solution.
FIG. 51.—Osmotic pressure of gelatin solution.

a beaker containing dilute acid solution of the same kind as was used in making up the gelatin solution. When osmotic equilibrium was established, the level of solution in the manometer was recorded and plotted against the pH value of the gelatin solution.[33] The measurements were made at 24°.

The explanation of the parallelism between the curves for swelling, viscosity, and osmotic pressure as functions of pH value is that

[33] Donnan Equilibrium and the Physical Properties of Proteins; II, Osmotic Pressure. Jacques Loeb. *J. General Physiol.* 3 (1921), 691.

the variation in each case is due to the same fundamental cause, namely, the establishment of a Donnan equilibrium. In the viscosity measurements, the solutions contain aggregates of gelatin molecules capable of swelling with change of pH value and, since the viscosity must increase with the increasing volume occupied by the gelatin, we should



Variables as Functions of Concentration of Added Salt.

FIG. 52.—Volume of powdered gelatin.
FIG. 53.—Viscosity of gelatin suspension.
FIG. 54.—Osmotic pressure of gelatin solution.

expect the viscosity to rise and fall with the degree of swelling of the gelatin particles.

In the experiments on osmotic pressure, we have an application of the Donnan equilibrium which is considerably simpler than that involved in the swelling of jellies, although of a similar kind.

In the swelling and osmotic pressure experiments, we note that the points of maximum given by sulfuric acid are only half as great as those given by hydrochloric acid, which is in harmony with the theory, since the divalent sulfate ion has no greater diffusion pressure than

the monovalent chloride ion and is only half as numerous for equivalent concentrations of gelatin salt.

In Figs. 52, 53, and 54 are given curves showing the depressing effect of increasing concentration of neutral salt upon the volume of powdered gelatin,[34] the viscosity of a suspension of powdered gelatin,[34] and the osmotic pressure of a solution of gelatin.[35] Again we find a parallelism in the results that would be expected from the theory.

Osmotic Pressure and Membrane Potentials.

A discussion of the mechanism of the osmotic pressures exerted by protein solutions may serve to make the theory of swelling, which is the more important in leather chemistry, a little clearer. The collodion bags used in Loeb's experiments were permeable to water and simple acids, bases, and salts, but not to dissolved proteins. Let us consider a solution of gelatin chloride and hydrochloric acid contained in a collodion bag which is brought into contact with pure water. Hydrochloric acid diffuses out through the membrane until equilibrium is established between the external solution and the gelatin solution inside the bag. The outside solution contains only hydrochloric acid, but the inside solution contains both hydrochloric acid and gelatin chloride. At equilibrium, in the outside solution, let

$$x = [H^+] = [Cl']$$

and in the inside solution let

$$y = [H^+]$$
$$z = [\text{gelatin ion}]$$

whence $$[Cl'] = y + z.$$

It is apparent from the reasoning given early in this chapter that at equilibrium

$$x^2 = y(y + z)$$

and that $$2y + z > 2x.$$

The greater concentration of diffusible ions of the inside solution, $2y + z$, must give rise to an osmotic pressure proportional to the quantity e in the expression

$$e = 2y + z - 2x.$$

This assumes that the gelatin exerts no osmotic pressure of its own, which may not be strictly true. A correction would have to be made by adding to e an amount corresponding to the osmotic pressure of the gelatin. But Loeb[36] has shown that any such correction that may be necessary is less than the probable experimental error of measurement.

[34] Donnan Equilibrium and the Physical Properties of Proteins; III, Viscosity. Jacques Loeb. *J. General Physiology* 3 (1921), 827.

[35] Donnan Equilibrium and the Physical Properties of Proteins; I, Membrane Potentials. Jacques Loeb. *J. General Physiol.* 3 (1921), 667.

[36] The Interpretation of the Influence of Acid on the Osmotic Pressure of Protein Solutions. Jacques Loeb. *J. Am. Chem. Soc.* 44 (1922), 1930.

When *x*, *y*, and *z* are determined in the solutions, the osmotic pressure can be calculated. At 24° C. the osmotic pressure, in terms of millimeters pressure of a column of water, equals $2.5e \times 10^5$. For casein chloride, Loeb found that the observed osmotic pressure approximated the value 250000*e* as closely as the determinations could be made.

Because of the unequal distribution of ions between the inside and outside solutions, there must be an electrical difference of potential set up between the two solutions whose measure at 20° C., as in the case of the jellies, is given by the formula

$$P.D. = 58(\text{pH inside minus pH outside}) \text{ millivolts.}$$

In determining the potential difference between the inside and outside solutions, Loeb used an apparatus similar to that shown in Fig. 47. The collodion bag containing the inside solution was hung in the beaker filled with the external solution. The manometer tube of the collodion bag was replaced by a funnel. The capillary tube of the right hand calomel cell was dipped into the funnel so as to make contact with the inside solution. The potential difference of the system was then measured by means of a Compton electrometer.

TABLE XV.

GELATIN SOLUTIONS AT 24° C.

Moles $NaNO_3$ per liter	Osmotic pressure (mm.)	pH value of Inside solution (a)	pH value of Outside solution (b)	(a) minus (b)	P.D (millivolts) Calculated	P.D (millivolts) Observed
None	435	3.58	3.05	0.53	31.2	31
0.000244	405	3.56	3.08	0.48	28.3	28
0.000488	371	3.51	3.10	0.41	24.0	24
0.000975	335	3.46	3.11	0.35	20.7	22
0.00195	280	3.41	3.14	0.27	16.0	16
0.0039	215	3.36	3.17	0.19	11.2	12
0.0078	134	3.32	3.20	0.12	7.0	7
0.0156	85	3.29	3.22	0.07	4.1	4
0.0312	63	3.25	3.24	0.01	0.6	0

Further quantitative proof of the correctness of the theory is furnished by the data in Table XV, showing the depressing effect of increasing concentration of neutral salt upon the osmotic pressure and potential difference of a system in which an acid solution of gelatin is separated from a gelatin-free solution by means of a collodion membrane.[37] The osmotic pressure curve is plotted in Fig. 54. When equilibrium was established, the pH values of both inside and outside solutions were determined and the potential differences were determined in the manner described above. The potential differences were also calculated from the pH determinations, the factor 58.8 being used for 24°. The agreement between calculated and observed results is as nearly perfect as could be hoped for.

[37] The Colloidal Behavior of Proteins. Jacques Loeb. *J. General Physiol.* 3 (1921), 557.

With increasing concentration of salt, the pH values of the inside and outside solutions approach each other. According to the theory, the distribution of any ion between the two solutions is similarly affected by the addition of salt; *i.e.*, the logarithms of its concentration in the inside and outside solutions, respectively, approach each other, bringing about a lessening of the difference in total concentration of diffusible ions between the two solutions. It is this effect rather than any supposed repression of ionization of the protein salt that is responsible for the reduction in the swelling of jellies and the osmotic pressure, viscosity, and potential difference of protein systems.

Changes in Viscosity of Gelatin Solutions with Time.

When hot solutions of gelatin are allowed to cool, their viscosities increase with time until they finally set to rigid jellies. Loeb attributes this to the formation of aggregates of gelatin molecules, the viscosity increasing with the average size of the gelatin particles. The curves in Figs. 55 and 56 show that this increase in viscosity with time

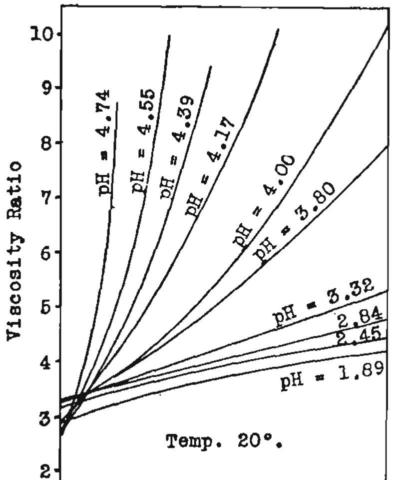


FIG. 55.—Increase in viscosity with time of 2-per cent solutions of gelatin sulfate of different pH values.

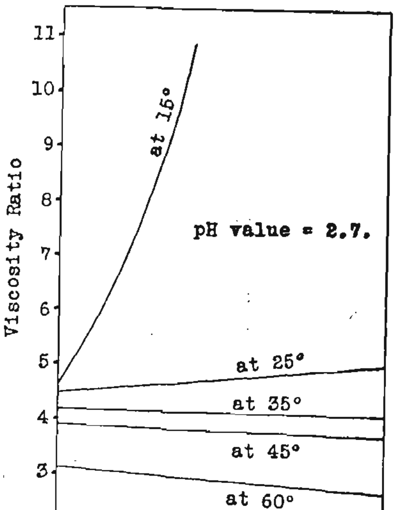


FIG. 56.—Change in viscosity with time of 2-per cent solutions of gelatin chloride at different temperatures.

is materially influenced both by the pH value and temperature of the gelatin solution.[88] The effect of pH value was determined by rapidly heating 2-per cent gelatin solutions containing different amounts of sulfuric acid to 45° C., cooling rapidly to 20°, and then maintaining

[88] The Reciprocal Relation between the Osmotic Pressure and the Viscosity of Gelatin Solutions. Jacques Loeb. *J. General Physiol.* 4 (1921), 97.

this temperature while viscosity measurements were made at intervals of 5 or 10 minutes. An increasing concentration of acid tends to prevent the formation of aggregates; the viscosity increases most rapidly at the isoelectric point.

The effect of temperature was determined by rapidly heating 2-per cent gelatin chloride solutions having a pH value of 2.7 to 45° C., cooling rapidly to the temperature at which the viscosity measurements were to be made, and maintaining this temperature while determinations were made at intervals of 5 or 10 minutes. The remarkable point to be observed is that the viscosity increases with time at temperatures below 35° C., but decreases with time at higher temperatures.

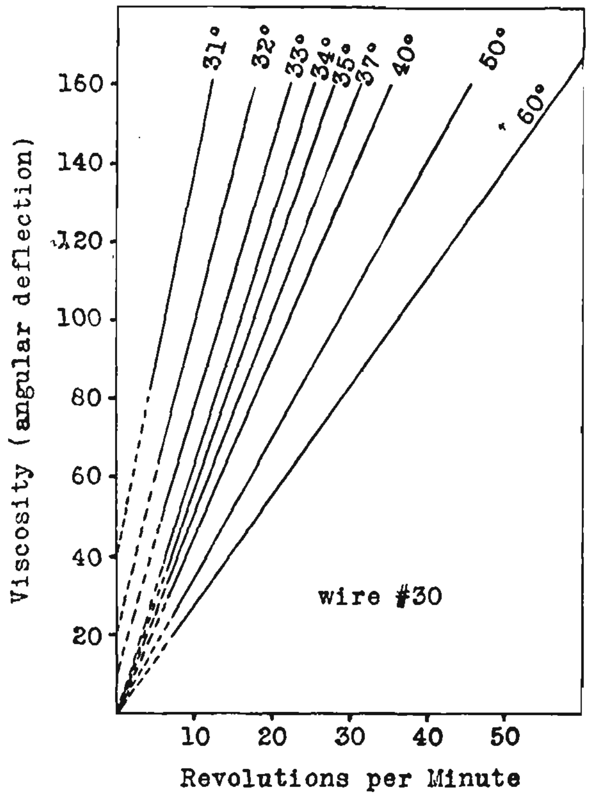


FIG. 57.—Viscosity-plasticity curves for a 20-per cent gelatin solution.

Bogue [39] measured the viscosities of gelatin solutions at different temperatures by means of a Macmichael torsional viscosimeter. At each temperature he made measurements for a number of different speeds of rotation of the cup. A set of these is shown in Fig. 57.

[39] The Sol-Gel Equilibrium in Protein Systems. R. H. Bogue. *J. Am. Chem. Soc.* 44 (1922), 1313.

The continuous lines cover the range of actual observation and the dotted portions represent the curves extrapolated to zero speed of rotation. For all temperatures above 34° C. the extrapolated curves pass through the origin, indicating truly viscous flow. But for lower temperatures, the curves do not pass through the origin; they indicate a finite deflection for an infinitesimal speed of rotation, showing that here we have an example of plastic flow. The gelatin solutions at lower temperature actually possess a measurable degree of rigidity. This is further evidence in support of Smith's view that at temperatures above 35° gelatin in solution exists in a form having no power of gelation. As the temperature is lowered, some of this sol form changes into a gel form which has the power of gelation. As the temperature is lowered, the proportion of gel form to sol form increases until at 15° and lower temperatures all of the gelatin exists in the gel form. The structure of the aggregates of molecules of the gel form is such as to impart to the solution the rigidity observed by Bogue.

When an acid solution of gelatin contained in a collodion bag at 20° C. is brought into equilibrium with a pure aqueous solution of the acid, the solution actually is separated into 3 phases. The gelatin solution within the bag has a hydrogen-ion concentration less than that of the external solution, but greater than that of the solution absorbed by the aggregates of gelatin molecules suspended in the gelatin solution. Loeb [37] has shown that, with increasing proportion of aggregates to dissolved gelatin, the variation of pH value produces an increasing effect upon viscosity, but a decreasing effect upon osmotic pressure measurements, as would be expected.

Theory of Salting Out and the Stability of Colloidal Dispersions.

Protein solutions and other so-called emulsoid colloids differ from the suspensoid colloids, such as colloidal gold, in requiring relatively very high concentrations of salt to precipitate their sols. It is generally admitted that the stability of colloidal dispersions is increased by the electrical charge usually associated with the particles. However, but little quantitative work has been done on the actual determination of this charge.

Powis [40] measured the potential difference at the oil-water boundary of an emulsion of cylinder oil and found that the emulsion was stable only when the absolute value of the potential difference exceeded 30 millivolts. When it was reduced to any value lying between plus or minus 30 millivolts, coagulation took place, but at a rate which was independent of the voltage.

It was pointed out by the author [41] in 1916 that Donnan's theory of membrane potentials is applicable to suspensoids as well as to protein jellies. A gold sol may be taken as a typical example. When gold is dispersed in water, the presence of chloride, bromide, iodide, or

[40] The Relation between the Stability of an Oil Emulsion and the Potential Difference at the Oil-Water Surface Boundary and the Coagulation of Colloidal Suspensions. F. Powis. *Z. physik. Chem.* 89 (1914), 186.

[41] Theory of Colloids. J. A. Wilson. *J. Am. Chem. Soc.* 38 (1916), 1982.

hydroxide ion in concentrations ranging from 0.00005 to 0.005 normal has a marked stabilizing effect on the sol produced and the particles are negatively charged. The effect seems to be due to the ability of these ions to form stable compounds with the gold. Fluoride, nitrate, sulfate, and chlorate ions decrease the stability of gold sols, which is significant in view of the fact that they do not form stable compounds with gold.[42]

In Fig. 58 let A and B represent two gold particles stabilized by potassium chloride. In combining with the gold, the chloride ions have imparted their negative charges to the particles. But the potassium ions are still left in solution, although their field of motion is restricted to the thin film of solution wetting the particles because they must continue to balance the negative charges on the particles. The volume

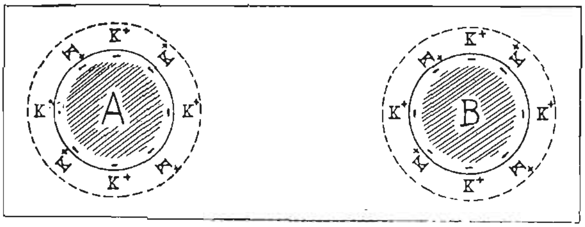


FIG. 58.—Particles of stable gold sol showing enveloping films of aqueous solution.

of the film of aqueous solution enveloping a particle will be measured by the surface area of the particle and the average distance that the potassium ions are able to travel from the surface.

Let us now consider the case where an amount of potassium chloride is present in the sol too small to cause precipitation. The enveloping film will contain potassium ions balancing the charges on the particles as well as ionized potassium chloride. The surrounding solution will have potassium and chloride ions only in equal numbers. In the surrounding solution let

$$x = [K^+] = [Cl']$$

in the enveloping film let

$$y = [Cl']$$

and $z = [K^+]$ balanced by charges on the particles,

whence $y + z$ represents the total concentration of potassium ion.

As was shown in the discussion of Donnan's theory, the product $[K^+] \times [Cl']$ must have the same value both in the enveloping film and in the surrounding solution at equilibrium. Hence

$$x^2 = y(y + z).$$

[42] The Electrical Synthesis of Colloids. H. T. Beans and H. E. Eastlack. *J. Am. Chem. Soc.* 37 (1915), 2667.

The surface layer of solution will have a greater concentration of ions than the surrounding solution by the amount $2y + z - 2x$. This unequal distribution of ions will give rise to a difference of potential between the enveloping film and the surrounding solution whose measure is

$$E = \frac{RT}{F} \log \frac{x}{y} = \frac{RT}{F} \log \frac{2x}{-z + \sqrt{4x^2 + z^2}}$$

But now, if we increase x without limit while z remains constant, E must decrease, approaching zero as a limit, since

$$\lim_{x = \infty} E = \frac{RT}{F} \log \frac{2x}{\sqrt{4x^2}} = 0.$$

It is thus evident that the difference of potential between the enveloping film and the surrounding solution will be a maximum when there is no free potassium chloride present and will decrease, approaching zero, as the concentration of potassium chloride is increased without limit.

The particles shown in Fig. 58 are prevented from coalescing because there is a sufficiently high potential difference of the same sign

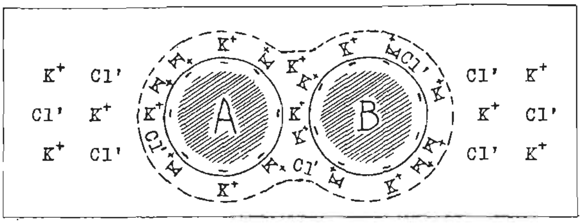


FIG. 59.—Coagulation of gold sol initiated by reduction of potential difference between enveloping films and the surrounding solution, by the addition of potassium chloride.

between the surrounding solution and each enveloping film. The electrostatic repulsion is determined by this potential difference rather than by the absolute electrical charge on the particles because the surface film completely envelops the particles and endows them with its own properties.

When enough potassium chloride has been added to lower the potential difference to a point where it is no longer able to overcome the attractive forces between the particles and the surface tension of the enveloping film, the particles move toward each other and the enveloping films of two or more particles blend into one, as shown in Fig. 59. It is at this point that the actual charges themselves come into play and probably determine the nature of the precipitate.

We have now only to substitute for the solid particle with its enveloping film the molecular network with aqueous solution filling up the interstices to make this theory of salting out apply to gelatin and similar proteins.

By referring back to Loeb's data in Table XV, it will be noted that the potential difference between an acid solution of gelatin and a gelatin-free solution with which it was in equilibrium was reduced to less than one millivolt by the addition of 0.031 mole per liter of sodium nitrate. If we may assume a similar lowering of potential difference between highly dispersed gelatin particles and the dispersion medium by the addition of this quantity of salt, it would follow that coagulation as a function of this difference of potential is not independent of the properties of the disperse phase. A gelatin solution shows no tendency to precipitate in the presence of 0.03 mole of sodium nitrate, but Powis found that his emulsion of cylinder oil ceased to be stable when the potential difference was reduced to 30 millivolts. Half-saturating a gelatin solution near the neutral point with ammonium sulfate will cause its precipitation, but we have as yet no data indicating the extent to which the potential difference is lowered before the precipitation begins.

Thomas[43] has called attention to the fact that the stability of colloidal dispersions may be determined more, in some cases, by the attraction between the dispersed phase and dispersion medium than by the difference of potential at the interface. The low degree of attraction between oil and water was probably responsible for the coagulation of Powis' emulsion at 30 millivolts. Apparently a potential difference of less than one millivolt is sufficient to prevent the precipitation of certain protein solutions because of the attraction existing between the protein and water. The attraction between sugar and water appears to be so great that no potential difference at all is required to keep it in solution.

Loeb's work, taken in conjunction with investigations in the author's laboratories, indicates that the lowering of the potential difference of protein systems is not brought about by repression of ionization of the protein salts, as has often been supposed, but rather by the mechanism of the Donnan equilibrium just described. In gelatin systems in which the potential difference has been lowered to a very small value, we find no repression of ionization of gelatin chloride measurable by means of calomel electrodes. Moreover, there is no need to postulate such repression in order to account quantitatively for the observed results.

An application of this theory of salting out to soap solutions furnishes a needed addition to McBain's[44] theory of soap solutions, in which it would be well also to look upon the micelle as an aggregate of monovalent ions rather than as a complex polyvalent ion.

[43] The Solution Theory of Colloidal Dispersion. A. W. Thomas. Lecture before the Milwaukee Section of the American Chemical Society, September 15, 1922.

[44] Colloidal Electrolytes. Soap Solutions and Their Constitution. J. W. McBain and C. S. Salmon. *J. Am. Chem. Soc.* 42 (1920), 426.

Adsorption.

Ever since Gibbs showed that the concentration of the solute must be greater at the surface than in the bulk of solution where the solute lowers the surface tension of the solution, there has been a tendency to look upon this proof as an explanation of the fact that substances of great specific surface reduce the concentration of solute in many different kinds of solution with which they are brought into contact. The error in this tendency lies in the fact that Gibbs' work applies only to the lowering of the surface tension by a substance actually in solution. Since, in many cases, it has not been found possible to determine the actual concentration of solute in the layer of solution immediately in contact with the surface of the material causing a decrease in concentration of solute in the bulk of solution, any conclusions as to the causes of such decrease have been open to question. In the case of gelatin, however, it has been found possible to measure concentrations in the absorbed solution and this has thrown considerable light on the phenomenon known as adsorption.

Adsorption is a term now widely used to indicate the removal of solute from solution by a material in contact with the solution. An empirical formula was proposed by Freundlich[45] which agrees approximately with some observed results over limited ranges, provided the two constants required in the formula can be selected to suit the findings. The formula may be represented as follows:

$$w = ax^b,$$

where w is the amount of solute removed from solution by unit quantity of the adsorbing material, x is the final concentration of solute, and a and b are constants selected to suit the occasion. Freundlich mentions that b may vary from 0.1 to 0.5, but a very much more.

The very nature of the equation makes it capable of fitting a great variety of data, especially since the constants may be selected as desired, but it doesn't explain anything. Referring back to Table XI, we find that the total quantity of chloride in the gelatin jelly at equilibrium, represented by $V(y + z)$, can be represented as a function of the hydrogen-ion concentration by the use of Freundlich's formula. Letting $V(y + z) = 7.33x^{0.42}$, we can plot a curve for the total quantity of hydrochloric acid, combined and uncombined, which has been absorbed by the jelly that agrees fairly closely with both the calculated and observed results given in Table XI, although not quite so well as do the calculated and observed results with each other. Plotting $\log V(y + z)$ of the above equation against $\log x$, we get a straight line, but the observed results never give a perfectly straight line, but vary in the same directions as do the calculated results of Table XI.

The curve for the concentration of gelatin chloride shown in Fig. 42 also can be represented approximately by Freundlich's formula by letting $z = 0.10x^{0.3}$. The formula is a convenient means of represent-

[45] Kapillarchemie. H. Freundlich. Leipsic, 1909.

ing a reaction approximately over a limited range, which it is able to do merely because many variables give curves that are nearly parabolic in shape.

Adsorption, so far as it pertains to gelatin jellies, is a manifestation of chemical combination complicated by the separation of the solution into two phases. We see no reason for looking upon adsorption by other materials in any different light. In the case of suspensoids, we are dealing with two phases of the solution apparently analogous to those of gelatin systems, the film of solution enveloping the particles corresponding to the solution absorbed by the jelly.

For a more elaborate treatment of certain phases of modern theories of the physical chemistry of the proteins, the reader is referred to Loeb's "Proteins and the Theory of Colloidal Behavior" [46] and to Bogue's "Chemistry and Technology of Gelatin and Glue." [46]

[46] McGraw-Hill Book Co., New York, 1922.

Chapter 6.

Preservation and Disinfection of Skin.

Practically every country in the world supplies hides and skins for leather manufacture. The skins from large, fully grown animals are usually called *hides,* those from half grown animals of the larger variety *kips,* while those from small or very young animals, or those intended for furs, are called *skins.* For example, as the calf grows into a cow, its skin remains a skin until it reaches a weight of about 15 pounds in the wet state, when it becomes a kip, while it becomes a hide at about 30 pounds. These figures are necessarily arbitrary, but serve to indicate the general scheme of classifying skins according to size. A bull hide may weigh more than 100 pounds. A sheep skin always remains a skin because it never assumes great size. The skin of the full grown East Indian buffalo is called a kip because it is smaller than the ordinary cow hide. For convenience, the term skin is used in its general sense throughout this book to include hides and kips, except when referring to specific cases.

The fact that animals are generally raised and slaughtered for food rather than for purposes of leather manufacture makes the tanner's chief raw material a by-product of the packing industry. For this reason a decreasing consumption of leather has but little influence upon the continued supply of skins, although it does tend to lower their market value. On the other hand, a brisk demand for leather generally does not in itself stimulate the raising and slaughtering of cattle, but rather has the effect of increasing the vigilance against damage to the existing supply of skins by putrefaction, careless handling, or the ravages of insects. Raw skins are highly putrescible and, since a considerable period of time usually elapses between the slaughter and the first tannery operation, it is necessary to subject them to some method of preservation as soon as possible after flaying.

Salting.

The commonest method of preserving skins, where they do not have to be transported very long distances and where salt is reasonably cheap and plentiful, is salting or curing, as it is sometimes called. The skins are laid out flat, flesh side up, and covered with salt in amount equal to about one quarter of their weight. Often they are placed in piles so arranged that the sides are higher than the center, which keeps the brine from flowing away, but this is undesirable unless

the skins have previously been washed free from blood. Sometime they are soaked in a concentrated solution of salt first and then covere with dry salt. The object is to get the salt to diffuse completely throug the substance of the skins, which may require only a few days fo light skins or weeks for heavy hides. Each skin is then folded u[hair side out, and in this condition sent to the market.

Where the blood and lymph have been removed from the skin immediately after flaying and enough pure salt has been used t give a nearly saturated solution in the skins, putrefaction is reduce to an almost negligible degree and the skins may be kept for a lon time with comparative safety. Common salt is most widely used, bu sodium sulfate and other neutral salts are also effective and actuall used in some places.

Salt Stains.

A defect commonly found in salted skins is the appearance o peculiar stains, usually either rusty brown or greenish blue in colo which are sometimes very difficult to remove and only become in tensified and darkened through contact with sulfide-lime liquors o vegetable tan liquors, substantially lowering the market value of th leather. Because they are a source of loss and annoyance to the tanne efforts have been made, from time to time, to determine their caus and methods for preventing them. Some stains disappear when the un haired skins are pickled with a solution of sulfuric acid and salt, bu others are resistant even to this process as ordinarily conducted. Thes stains received the name salt stains from the general belief that the were caused by the salt used in curing. At any rate, it was ap preciated that their frequency of occurrence was influenced by th composition of the salt and the method of its application.

The percentage of stained skins was especially high in those part of Europe where edible salt is taxed and the salt used for curing mus be denatured. The use of commercial aluminum salts, particularl those containing iron, was looked upon with suspicion and the scientifi men of the industry began to seek other denaturing materials tha would tend to prevent rather than to cause stains.

One important school of thought regarded bacterial action as bein largely responsible for the formation of the stains and sought de naturing materials capable of checking bacterial growth. Paessler[1] found that the percentage of stains appearing on skins could be greatl reduced by curing with salt denatured with 3 per cent of its weigh of anhydrous sodium carbonate. His discovery was put into genera use and had the important effect of considerably decreasing th percentage of stained skins.

Schmidt[2] showed that bacterial action could be effectively checke by using salt previously sprinkled with a 12-per cent solution of zin chloride and this method has been used to some extent to prevent sal

[1] Salting of Hides and Skins. J. Paessler. *Ledertech. Rundschau* (1912), 137.
[2] Depreciation of Skins in Process. C. E. Schmidt. *Shoe & Leather Rep.*, Marcl 6, 1911.

stains. But, after making a series of comparative tests, Paessler[3] claimed that zinc chloride was no more effective than sodium carbonate in preventing salt stains.

Romana and Baldracco[4] suspected the blood and lymph as the source of the stains and tried washing the skins very thoroughly after flaying and before adding the salt. On skins thoroughly washed they found no stains at all. They also found that the stains could be prevented by adding to the salt used in curing 1 per cent of its weight of sodium fluoride.

Eitner[5] suggested that many stains are caused by delaying the salting operation until bacterial action has already considerably advanced. He advised a more thorough elimination of water by heavily salting the skins, draining off as much brine as possible, and then resalting. The brine drained off carries with it proteins which are very susceptible to putrefaction.

Yocum[6] observed that salt stains occurred much more frequently in summer than in winter and were most abundant where the skins had had greatest contact with the air or had been kept for the longest period in the salted condition. Tests for iron were obtained on pieces of filter paper previously moistened with acetic acid and placed on the stains. Where stains still appeared on the finished leather, he obtained a test for iron in the stained, but not in the unstained parts. But iron was often found in the ash of fresh skins which showed no stains when tanned at once without salting. This seemed to indicate that the staining was due to a change in the condition of the iron present which enabled it to combine with the skin. He was able to produce stains on skins by treating them with hemoglobin and suggested that the hemoglobin of the blood might have been the source of the staining material.

Becker[7] made extended studies of yellow, orange, and red stains on skins and isolated from them bacteria which, in pure cultures, were able to produce the corresponding stains. He also found that adding salt, up to 10 per cent of the weight of the skin, favored the action of these bacteria, while greater amounts retarded it. He warned against the use of an insufficient quantity of salt in curing, storing the skins in a warm, damp atmosphere, and of allowing dirt and filth to remain on the skins. As a means of preventing these stains, he recommended dipping the skins in a 0.25-per cent solution of mustard oil, followed by the application of plenty of clean salt denatured with sodium carbonate. Not being able to reproduce the blue stains by bacterial action alone, he admitted that these might be due to chemical changes other than those involving bacteria.

The great stress placed upon the rôle played by bacteria in the formation of salt stains adds interest to the work of Abt,[8, 9] who main-

[3] Soda as a Denaturant for Hide Salt. J. Paessler. *Ledertech. Rundschau* (1921), 169.
[4] Salting of Hides and Avoidance of So-Called Salt Stains. C. Romana and G. Baldracco. *Collegium* (1912), 533.
[5] Theory of Salt Stains. W. Eitner. *Gerber* (1913), serially.
[6] Salt Stains. J. H. Yocum. *J. Am. Leather Chem. Assoc.* 8 (1913), 22.
[7] Salt Stains. H. Becker. *Collegium* (1912), 408.
[8] Origin of Salt Stains. G. Abt. *Collegium* (1912), 388.
[9] Microscopical Examination of Skin and Leather Applied to the Study of Salt Stains. *Ibid.* (1914), 130.

tained that most of the salt stains he had examined in France were not caused by bacterial action. Particularly bad cases of staining were traced to the presence of crystals of calcium sulfate in the salt used for curing. The stains themselves always contained considerable quantities of calcium phosphate as well as iron. The stained regions always gave more intense qualitative tests for iron than the unstained regions, but analysis showed the same actual quantity of iron in both. He pictured the stain formation as follows: Calcium sulfate present in the salt used for curing is precipitated as phosphate through contact with ammonium phosphate derived from the nucleic acids of the skin. The ammonium sulfate thus liberated then reacts with insoluble ferrous carbonate, naturally occurring in the skin, forming the soluble ferrous sulfate, which forms a stain by combining with the skin protein.

Abt attempted to follow the progress of the staining under the microscope and found that the cell nuclei disappear as the staining increases. The connective tissues gradually disintegrate, but he could find no bacteria between the altered fibers, nor did the disintegration resemble the type of decomposition produced by bacteria. He thought the iron probably originated either in the chromatin of the cell nuclei or from the blood. A second type of stain contained no calcium phosphate, but the epithelial cells were strongly pigmented. These stains he regarded as due to the fixation of the pigment by mineral matter in such a way as to prevent its decomposition by the lime liquors later on. Abt also recommended adding sodium carbonate to salt to be used for curing because it precipitates the calcium salts present and also exerts an antiseptic and dehydrating action.

Although Abt contended that most of the stains which he had examined were not caused by bacterial action, he admitted that bacteria might play an important part in the formation of other types of stains. In fact, he [10] isolated an organism from one stain capable of producing a brown color on gelatin in the presence of traces of calcium phosphate and iron.

At least three different explanations have been offered to account for the effectiveness of sodium carbonate in preventing salt stains. Abt attributed it to the precipitation of calcium salts which might be present in the salt used for curing. Paessler and others looked upon it as due to the production of an alkalinity unfavorable to the action of the bacteria thought to be responsible for the stains. Moeller,[11] however, suggested that the staining is a tanning action, due to such agents as the melanins or to iron and sulfur bacteria, but that this tanning action cannot proceed in alkaline solution. It is, of course, obvious that the sodium carbonate has the important effect of preventing iron salts from passing into solution, in which condition they would be free to combine with the skin forming the stains.

Summing up the work of various investigators, it would appear that salt stains are of several kinds and may be produced directly by bacteria, such as Becker's chromogenic organisms, or by soluble iron

[10] Rôle Played by Bacteria in Production of Salt Stains. *Collegium* (1913), 204.
[11] Origin of Salt Stains. W. Moeller. *Collegium* (1917), serially.

salts. These iron salts may be introduced in the salt used for curing or may be formed from the insoluble iron salts already present in the skin, either by chemical action, as described by Abt, or through the intervention of bacteria. The blood and lymph of skins furnish an excellent medium for bacterial growth and contain compounds of both iron and phosphates.

The following simple rules represent the best means known to the author for preventing these undesirable stains and, it would seem, ought to be quite effective, if carefully observed at the point of slaughter. Immediately after flaying, the skins should be washed very thoroughly in running water to remove as much blood, lymph, and other soluble matter as possible and then salted uniformly in all parts with plenty of clean salt, free from iron and containing about 4 per cent of its weight of anhydrous sodium carbonate. During the time required for the salt to diffuse completely through the skins, they should be kept in a cool place and the brine formed should be allowed to drain away, carrying with it any soluble proteins not previously washed out. Salt equal in amount to at least one quarter of the weight of the skins should be used. Proper curing of skins is necessary, not only to prevent the formation of stains, but also to prevent putrefaction that would otherwise impair the yield and substance of the leather.

Drying.

In tropical countries, like Java and India, from which skins are often transported very long distances, the simplest and most economical method of preserving skins is to dry them. This is true for all regions where salt and antiseptics are scarce. Moreover, drying reduces the weight of the skin by about 70 per cent. In the absence of moisture, putrefactive bacteria are practically without action on the skin proteins, although the drying does not always kill the bacteria.

When this method of preserving skins is intelligently controlled, very little damage to the skin results. In hot climates, care must be exercised to prevent excessive heating of parts of the skin which are still wet or the protein matter may decompose. Sometimes skins are dried so rapidly that the outer layers feel quite dry, while the interior is still moist enough to permit putrefaction. Skins packed and shipped in this condition are liable to considerable damage. Defects of this kind usually cannot be detected until the tanner attempts to soak the skins back, when they may actually disintegrate or the grain and flesh layers may tend to separate, due to the hydrolysis of the protein matter in the interior. If the drying has been unduly prolonged at high temperatures, the tanner may have considerable difficulty in soaking the skins back to their normal water content.

The skin tissues continue to live for some time after the death of the animal and, in the living condition, are not readily subject to putrefaction. It is therefore desirable to dry skins as soon as possible after flaying. They should first be cleansed thoroughly by washing away all the blood and lymph and then suspended freely in a current

of cool air until dry. Where conditions are such that drying cannot be effected sufficiently rapidly to prevent putrefaction, as in damp climates, it is customary to treat the skins first with some antiseptic, such as naphthalene, which acts also to protect the skins against the attacks of insects during drying.

The advantages of drying, as a means of preserving skins, are simplicity and speed of operation, independence of a supply of preservative material, and low transportation costs for the skins. The disadvantages are the difficulty of wetting the skins back later to their normal water content, the almost impossibility of detecting damage to the skin proteins until they are wet back, and the fact that dried skins may carry disease-producing bacteria or their spores in a form likely to spread infection.

Salting and Drying.

Sometimes the methods of salting and drying are combined to advantage. The skins are first salted in the usual manner, the brine is allowed to drain away, and they are then allowed to dry slowly. The salt has the effect of hindering putrefaction during the drying.

This method is extensively used in some parts of India, but the salt used is a native earth which, according to Procter,[12] consists chiefly of sodium sulfate mixed with sand containing insoluble compounds of iron and aluminum. This material is made into a very thin paste, which is brushed onto the flesh side of the skins. Next day more of the paste is rubbed onto the flesh side of the outstretched skin and rubbed into it with a porous brick. After 3 or 4 saltings, the skins are dried under cover and are ready for export. The iron present in the salt sometimes causes a staining of the skins when they are kept for a long time in a moist atmosphere.

Pickling.

Skins may be preserved by pickling in a solution of sulfuric or hydrochloric acid and sodium chloride. A solution made about N/20 as to acid and 2N as to salt is efficient. This method is not in general use for fresh skins because of the complications involved in attempting to bring them into an alkaline condition later on for unhairing. But for sheep skins, already dewooled, it is a widely used method and convenient, because the skins are then ready for chrome tanning without further treatment.

The value of this method for preserving sheep skins is increased by the fact that wool is often more valuable than the skin. The skins are frequently purchased by *wool pullers,* who remove the wool by methods to be described in Chapter 8, and then lime, bate, and pickle them, in which condition they are stored or resold to tanners. This method of preservation permits the immediate use of the wool without destroying the skin or forcing it directly into the tanning process.

[12] Principles of Leather Manufacture, 2nd edition. H. R. Procter. D. Van Nostrand Co., New York.

In pickling, the skins are usually thrown into a vat, equipped with a paddle wheel for keeping the liquor and skins well stirred and containing a strong solution of salt with a definite excess of sulfuric acid, which is controlled by analysis. The skins are left in the pickle liquor until equilibrium has been practically reached, which is determined by noting when there is little further decrease in concentration of acid with time. This may require anywhere from 4 to 24 hours, depending upon the thickness and condition of the skins and upon the equilibrium concentration of acid selected. Equilibrium is reached more quickly when more concentrated solutions of acid are used, but, if too strong a solution is used, it may be necessary to remove some of the acid prior to tanning by washing the skins in a concentrated neutral salt solution. After pickling, the skins are allowed to drain and are then stored in a damp condition until the tanner is ready to put them into process.

Disinfection.

Infectious diseases among cattle are common in many countries, particularly in Asia. For this reason some kind of disinfection of skins to be transported from infected areas is necessary in order to prevent the spread of disease germs. Much attention has been paid to preventing the spread of rinderpest, foot-and-mouth disease, and the much dreaded anthrax, which occasionally proves fatal to human beings infected with it. Various governments have issued rules to be followed in disinfecting skins from regions known to be infected. The greatest precautions have been directed against the spread of anthrax because of the danger to human life, but any treatment effective against this disease may be considered effective against the others as well.

Anthrax is the disease caused by the spore-bearing *bacillus anthracis*. The bacillus possesses a short rod-like form and is easily destroyed. According to Seymour-Jones,[13] drying alone will kill the rod bacillus. The spore, on the other hand, is very resistant to methods of disinfection that do not cause some injury to the skins, and it is this that makes the problem of disinfecting skins a difficult one. Anthrax spores have been found in dried skins and in blood clots on hair and wool, but seldom, if ever, in wet salted skins.

Practical methods of disinfection are limited because so many disinfectants are injurious to the skin and reduce its value for leather making. Consequently only a few workable methods have been devised. Of these, the best known is that of Seymour-Jones,[14] who recommends its employment at the point of export rather than of import because of the danger of spreading the disease during transit. It consists in soaking the dried skins for from 1 to 3 days in a 1-per cent solution of formic acid containing 0.02 per cent of mercuric chloride. They are then soaked for an hour in a saturated solution of common salt, drained, and baled for shipment.

[13] Anthrax Prophylaxis in the Leather Industry. Alfred Seymour-Jones. *J. Am. Leather Chem. Assoc.* 17 (1922), 55.
[14] Formic-Mercury Anthrax Sterilization Method. Alfred Seymour-Jones, London (1910).

Procter and Seymour-Jones[15] studied the rate of absorption of formic acid and mercuric chloride during the soaking operation at a number of different concentrations, using 1 liter of solution per 100 grams of dried skin. The concentration of acid in the solution always fell slowly during a period of 20 hours, but that of the salt at first increased and then dropped, finally approaching a limiting concentration. The initial increase in concentration of mercuric chloride was found to be the result of a greater initial rate of absorption or pene-

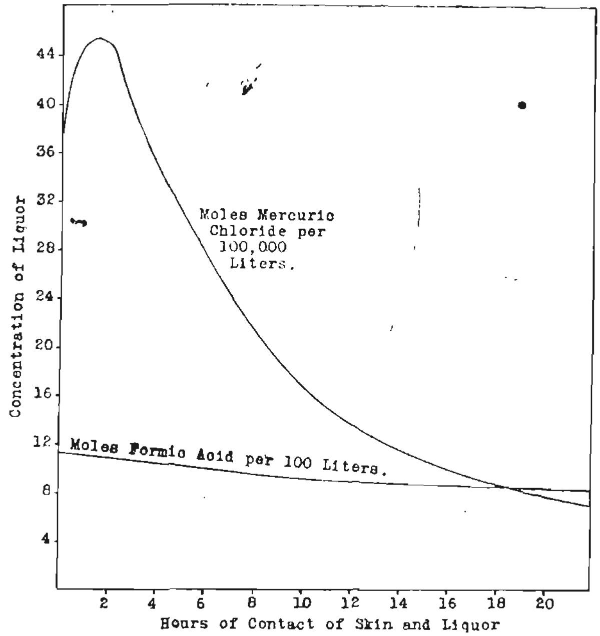


FIG. 60.—Change in composition of solution with time in the Formic-Mercury Process for sterilizing skins.

tration of water and acid than of the salt. The results of one of their experiments are shown in Fig. 60.

The absorption of water caused by the acid renders the skin almost as soft as in the fresh state and the subsequent immersion in saturated sodium chloride solution brings it into a condition resembling that of salted skins. Seymour-Jones points out that skins in this condition are not only properly disinfected, but that they present less of a gamble to the tanner because they show any defects in the skin that would not be visible when the skin is in the dried state.

Schattenfroh[16] proposed a method of disinfection involving the

[15] Seymour-Jones Anthrax Sterilization Method. H. R. Procter and Arnold Seymour-Jones. *Leather Trades Review* through *J. Am. Leather Chem. Assoc.* 6 (1911), 85.
[16] A Harmless Method for the Disinfection of Skins against Anthrax. A. Schattenfroh. *Collegium* (1911), 248.

soaking of infected skins in a solution containing 10 per cent of sodium chloride and 2 per cent of hydrochloric acid at 40° C. for 3 days. Much debate has waged over the relative merits of the Seymour-Jones and Schattenfroh methods. Tilley,[17] after experimenting with both methods, concluded that the Seymour-Jones process is effective, but only provided the concentration of mercuric chloride is as high as 0.04 per cent and the skins are not subjected within a week to treatment with sodium sulfide or other substance that would neutralize the disinfectant. It should, therefore, be effective where the disinfection is carried out at a foreign port before shipping. Seymour-Jones,[18] in reply, pointed out that neutralization of the disinfectant by sodium sulfide would take place only in the unhairing process, whereas, under conditions existing during this process, the sodium sulfide itself is a perfect sterilizer of anthrax spores. This would seem to eliminate any possible danger of anthrax infection from skin or leather that had passed through the usual lime and sulfide method of unhairing.

Tilley found the Schattenfroh method effective when the hides were allowed to remain in the acid-salt solution for 48 hours or longer. Schnurer and Sevcik,[19] however, applied the Schattenfroh process to very heavy hides and obtained 4 positive tests of infection out of 11 made after the hides had been in a solution containing 2 per cent of hydrochloric acid and 10 per cent of sodium chloride for 72 hours. They attributed the more favorable results obtained by Schattenfroh to the fact that he experimented with very thin skins. Using the Seymour-Jones process on very heavy hides, they found it necessary, in order to get complete sterilization in 24 hours, to increase the concentration of mercuric chloride to 0.2 per cent, but hides so treated were found by Eitner not to have suffered for tanning purposes. They also found it necessary to degrease heavy sheep skins before applying the Seymour-Jones process, as otherwise a ten-fold dose of mercuric chloride was required.

Seymour-Jones objected to the Schattenfroh method on the ground that it is workable only under laboratory conditions and that its factors of time, temperature, and general manipulation are not suited to practical operations. Ponder,[20] investigating methods of disinfection for the Leathersellers Company of London, and Abt,[21] of the Pasteur Institute, Paris, working for a syndicate of French tanners, both reported in favor of the Seymour-Jones process. Apparently neither process does any injury to the skins that can be detected in the finished leather, according to the findings of numerous investigators.

Abt, however, has pointed out that hides would contain no anthrax spores, if they were dried in the sun immediately after flaying, and this view is supported by Seymour-Jones.

[17] Bacteriological Study of Methods for the Disinfection of Hides Infected with Anthrax Spores. F. W. Tilley. *J. Am. Leather Chem. Assoc.* 11 (1916), 131.

[18] The Formic-Mercury Process for Sterilizing and Curing Dried Hides. Alfred Seymour-Jones. *J. Am. Leather Chem. Assoc.* 12 (1917), 68.

[19] Anthrax Disinfection of Hides. J. Schnurer and F. Sevcik. *Tierärztliches Zentralbl.* through *J. Am. Leather Chem. Assoc.* 8 (1913), 174.

[20] A report to Worshipful Company of Leathersellers, 1911. C. Ponder.

[21] Disinfection of Anthrax Infected Hides and Skins. Pasteur Institute, 1913. G. Abt.

Chapter 7.

Soaking and Fleshing.

As received at the tannery, skins contain much material unsuitable for leather manufacture and which would introduce serious complications, if not removed as early in the process as possible. For this reason every effort is made to remove each undesirable constituent as soon as it can be done efficiently. The preparation of skin for tanning is carried out in a department of the tannery known as the *beamhouse* and includes, not only the removal of the undesirable parts, but also the regulation of the degree of swelling of the skin proteins.

Ears, cheeks, hoofs, and tails are trimmed from skins still possessing them and the flesh, or adipose tissue, is removed by working the skin in a *fleshing machine,* which forces the flesh side of the skin against a revolving roller set with sharp blades, which cut away the adipose layer. The trimmings and fleshings make up the tannery by-product known as glue stock and are disposed of for manufacture into glue and gelatin.

On the hair side of the skin, the epidermis is made up of a network of membranes, forming the walls of the epithelial cells, impermeable to the soluble proteins of the skin as well as to other material having large molecules or consisting of aggregates of molecules, while on the flesh side the adipose tissue consists of layers of fat cells bound together by extensive series of semi-permeable membranes. It will, therefore, be readily appreciated why the adipose tissue must be removed before the skin can be thoroughly cleansed and freed from soluble protein matter.

The collagen fibers of the skin are joined together at the lower boundary of the derma in such manner as to give increased strength to the skin. In fleshing, it is important to remove all of the adipose tissue without cutting into the derma, which would weaken its structure as well as lower the leather yield. But reference to Fig. 7 will show that this is not difficult where the skin is in its normal state. The lower boundary of the derma is sharply defined and the adipose tissue is not joined securely to it at all points. But where the skin has undergone partial or complete drying, satisfactory fleshing becomes a more difficult operation.

During the ordinary methods of drying, protein jellies suffer a change of shape, as well as of size, depending upon their initial shape, the resistance offered to shrinkage in any direction, the rate of drying, and many other factors. This was prettily illustrated by Sheppard

and Elliott[1] with blocks of gelatin jellies. The photographs shown in Figs. 61 to 64 were kindly furnished by Dr. S. E. Sheppard of the Eastman Kodak Co. Fig. 62 shows four stages in the drying of a cube of 20-per cent gelatin jelly which was freely suspended in the air. No. 1 represents the original block of jelly, Nos. 2 and 3 intermediate stages in the drying, and No. 4 the dried block. At first the drying naturally proceeds most rapidly at the corners, or trihedral angles, and the faces of the cube become curved outward, as shown in No. 2, giving convex surfaces under tension. This is rapidly followed by the drying and hardening of the edges, forming a rigid framework, so that the bulk of the jelly now behaves as though suspended inside of a rigid wire frame. The faces now gradually recede and the edges become somewhat incurved until a sort of inner cube is formed with connected flanges reinforcing it, any cross-section through this having an I-beam structure, as though the drying proceeded in a manner developing the greatest resistance to stress. The flange-like edges appear to form sections of hyperboloids with a common focus at the center of the cube. Fig. 61 shows three stages in the drying of a sphere of gelatin jelly. Even here the drying is not uniform, but the surface becomes puckered and wrinkled.

The dried forms of two cylinders of gelatin jelly are shown in Fig. 64 and their end views in Fig. 63. One base of the first and both bases of the second cylinder were allowed to adhere to rigid surfaces during the drying. The shrinkage in area of these bases being prevented, the reduction in volume had to be compensated by greater shrinkage in other directions. In the drying of a thin coat of gelatin jelly on a glass plate, the shrinkage takes place almost entirely in the direction perpendicular to the plane of the glass surface.

Upon soaking dried blocks of gelatin in water, the swelling proceeds in the direction counter to that followed during drying and the blocks tend to assume the shapes and sizes they possessed before drying.

During the drying of skin, the distortions of shape suffered by the insoluble protein constituents are further complicated by the tendency for the fibers to adhere to each other. Before a skin can be fleshed satisfactorily, it is necessary to soak it in water long enough so that all of the insoluble protein constituents may swell to their normal sizes and shapes. When the skin is not uniformly swollen, the boundary between the derma and adipose tissue cannot be made to lie in a single plane. The fleshing machine would then cut the skin so as to leave the flesh side apparently smooth, but in so doing would either leave a considerable amount of adipose tissue on the skin to interfere with the proper cleansing of the skin or else injure the skin by cutting into the derma. The flesh side would look smooth enough upon coming from the machine, but would be ragged and irregular in thickness after the skin had been soaked further or swollen in the liquors used later. F. L. Seymour-Jones says that in Europe it is customary not to flesh

[1] The Drying and Swelling of Gelatin. S. E. Sheppard and F. A. Elliott. *J. Am. Chem. Soc.* 44 (1922), 373.

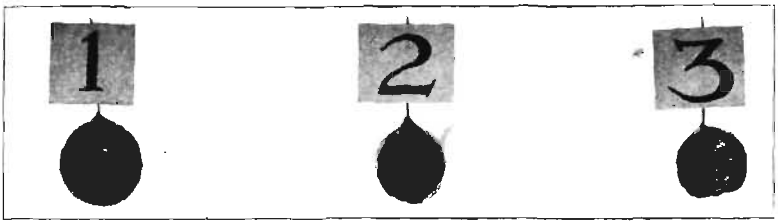


Fig. 61.—Three Stages in the Drying of a Sphere of Gelatin Jelly.

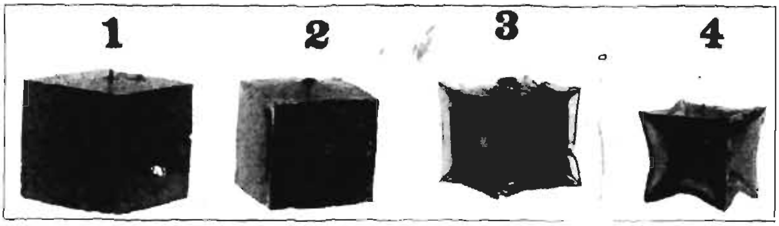


Fig. 62.—Four Stages in the Drying of a Cube of Gelatin Jelly.

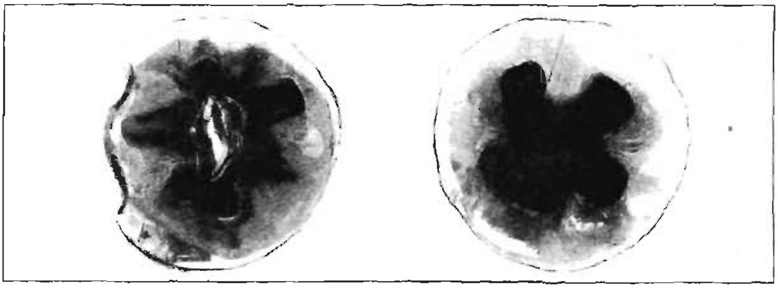


Fig. 63.—End Views of Dried Cylinders of Gelatin Jelly.

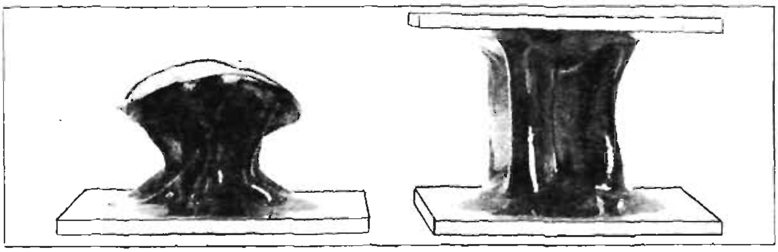


Fig. 64.—Two Cylinders of Gelatin Jelly Dried with One and Two Faces, Respectively, Adhering to Rigid Surfaces.

skins until after at least a preliminary liming. In America, tanners of goat skins usually flesh them after liming.

Heavy, dried hides not only require a more drastic treatment than light, fresh skins, but are also better able to stand it without injury to the resulting leather. In order to get better and more uniform results, the tanner sorts the skins he receives according to weight and general condition. A suitable number of skins, all as nearly alike as possible, are assembled into a unit lot and kept together throughout the process. The treatment is then determined by the average size and condition of the skins as well as by the kind of leather desired. Very large hides are often cut into two *sides* along the line of the back bone, for convenience in handling.

Where the skins come to the tannery in a perfectly fresh condition, the soaking and fleshing operations are extremely simple. After the skins have been trimmed, the adhering blood and dirt are removed by tumbling the skins for half an hour or more in an open drum through which water is flowing. They are then fleshed, after which they are soaked in several changes of clean, cold water containing salt or a small quantity of alkali, the object of which is to free them from soluble protein matter that would otherwise contaminate the liquors used to loosen the hair and epidermis. The purpose of the salt, or alkali, is to render the globulins soluble so that they may be removed along with the albumins.

For dried, or partially dried, skins it is necessary to soak the skins both before and after the fleshing operation. The first soaking is primarily for the purpose of swelling the insoluble proteins back to their normal sizes and shapes so that the fleshing operation may be carried out efficiently. The second soaking is for the purpose of freeing the skin from soluble protein matter.

The time required for the first soaking depends upon the extent to which the skins have been dried. Completely dried skins absorb cold water extremely slowly. Since skins, as received at the tannery, are almost invariably contaminated with proteolytic bacteria, the use of warm water in soaking is somewhat risky, unless the process is very carefully watched. It is usually preferable to hasten the swelling of dried skins by adding small quantities of acid or alkali to the soak waters.

Because of the attention centered on the Seymour-Jones process of disinfecting skins, described in the preceding chapter, formic acid has often been used as a swelling agent, although other acids can be used equally as well by applying a simple system of chemical control. Alkalies, however, are more suitable where the skins are subsequently to be treated with alkaline liquors to loosen the hair. Sodium sulfide is most commonly employed to swell dried skins because it requires less careful control than the use of more caustic materials, such as sodium hydroxide. In soaking, a gallon of water is usually used per pound of wet skin or for one-fifth of a pound of completely dried skin. Making the initial concentration of alkali about 0.02 normal is usually enough to initiate the swelling without causing damage either to the skin or the hair. The

solution after using is then only very faintly alkaline, the greater portion of the alkali having combined with the protein matter. The alkaline liquor is used only for the first soaking after which the skins are moved into fresh water each day until swollen to normal.

Sometimes the absorption of water and softening of the skins is assisted by tumbling them in revolving drums with water between successive soakings. This is usually done with heavy, dried hides or sides.

As a rule, salted skins can be fleshed after soaking for only one day, or less. After fleshing, it has been the custom to soak the skins in successive changes of water until practically all of the salt has been removed. The salt diffuses out from the skin much more rapidly than the soluble protein matter, so that continuing the soaking until all of the salt has been removed is not unduly prolonging the process where it is desirable to free the skin as far as possible from soluble protein matter. This custom, however, has created a widespread, but erroneous, impression that it is dangerous to carry salt into the lime liquors. On the contrary, salt assists in the unhairing and plumping of skins by the ordinary lime liquor. Its action in this respect appears to be due to the fact that it increases the hydroxide-ion concentration of alkaline solutions in general.[2]

Defects in finished leather are often traceable to the soaking operation. Although bacterial action is the chief source of danger, the skin may suffer from other causes. The tissues of the body do not necessarily die with the animal, but may continue to live for an indefinite period, if sufficiently well supplied with nourishment. For this reason it is conceivable that the sudden chilling of a fresh skin may exert an effect upon the muscles and glands of the thermostat layer. If, for example, the erector pili muscles were suddenly contracted and paralyzed by chilling, the result would be a permanent roughening of the surface of the skin. There have been cases where an unusual roughness of the grain surface of leather seemed to result from the sudden immersion of the warm skins, before tanning, in water near the freezing point. But the danger from proteolytic bacteria makes the use of warm water undesirable for soaking. Cold water should be used, but the operations should be so conducted that the temperature of the skins falls gradually.

How long the various parts of the skin continue to live and function after the animal has been flayed remains to be determined. We do know, however, that the skin undergoes changes of one sort or another practically from the moment of flaying. McLaughlin[3] noted that the rate of swelling of hide in saturated lime water decreases during the first two or three hours following the flaying of a freshly killed animal. A strip of hide put into lime water containing undissolved lime in excess 30 minutes after flaying swelled about 30 per cent more in 120

[2] The Hydrogen- and Hydroxyl-Ion Activities of Solutions of Hydrochloric Acid, Sodium and Potassium Hydroxides in the Presence of Neutral Salts. H. S. Harned. *J. Am. Chem. Soc.* 37 (1915), 2460.

[3] Post-Mortem Changes in Hide. G. D. McLaughlin. *J. Am. Leather Chem. Assoc.* 16 (1921), 435.

hours than a corresponding strip put into the lime water 210 minutes after the flaying.

This is, of course, not surprising in view of the fact that many changes are known to occur in skin, after the death of the animal, all of which would tend to retard the swelling in lime water. The coagulation of the blood, during which fibrinogen is converted into fibrin, would tend to retard the penetration of lime into the skin and the partial drying of some of the tissues would act in a similar manner. Decomposition of some of the protein constituents would yield simpler bodies capable of forming salts of calcium, which would serve to repress the swelling of the proteins by calcium hydroxide. It is possible also that some of the proteins capable of swelling are gradually broken down into simpler bodies not having the power to swell.

Where the preservation of a skin has been done carefully and intelligently, these changes appear not to have any detrimental effect upon the leather produced. The author has tested this by comparing the tannage of skins properly preserved and kept for months before tanning with the tannage of skins put into process within an hour of the death of the animals: no appreciable differences could be detected by chemical, physical, or microscopical examinations of the final leathers. But where there is carelessness in handling, the skins may suffer irreparable damage before the soaking operation has been completed.

The commonest source of danger in soaking is bacterial action. Although the inner surface of the skin on the living animal may be free from bacteria, it acquires them from the atmosphere very rapidly from the instant of flaying and acts as an ideal medium for the reproduction of bacteria. By the time the skin reaches the soak vats, it is usually contaminated with countless millions of bacteria. Many species of these bacteria are known to secrete enzymes, which may prove as harmful as the bacteria themselves. The chief practical object to be gained from a study of the bacteria common to tannery soak waters is to find means of destroying them, or at least of preventing them from doing any damage to the skins. An extensive series of investigations of the bacteria and enzymes present in tannery liquors has been made by Wood.[4]

Andreasch[5] isolated a number of species of bacteria from tannery soak liquors of which he identified the following:

Bacillus fluorescens liquefaciens (Flügge).
B. megaterium (de Bary).
B. subtilis.
B. mesentericus vulgatus.
B. mesentericus fuscus.
B. mycoides (Flügge).
B. liquidus (Frankland).
B. gasoformans (Eisenberg).

[4] Properties and Action of Enzymes in Relation to Leather Manufacture. J. T. Wood. *J. Ind. Eng. Chem.* 13 (1921), 1135.

[5] *Der Gerber*, 1895-6; *J. Soc. Chem. Ind.*, 1896-7.

White bacillus (Maschek).
Proteus vulgaris.
Proteus mirabilis.
B. butyricus (Hueppe).
White streptococcus (Maschek).
Worm shaped streptococcus (Maschek).
Grey coccus (Maschek).

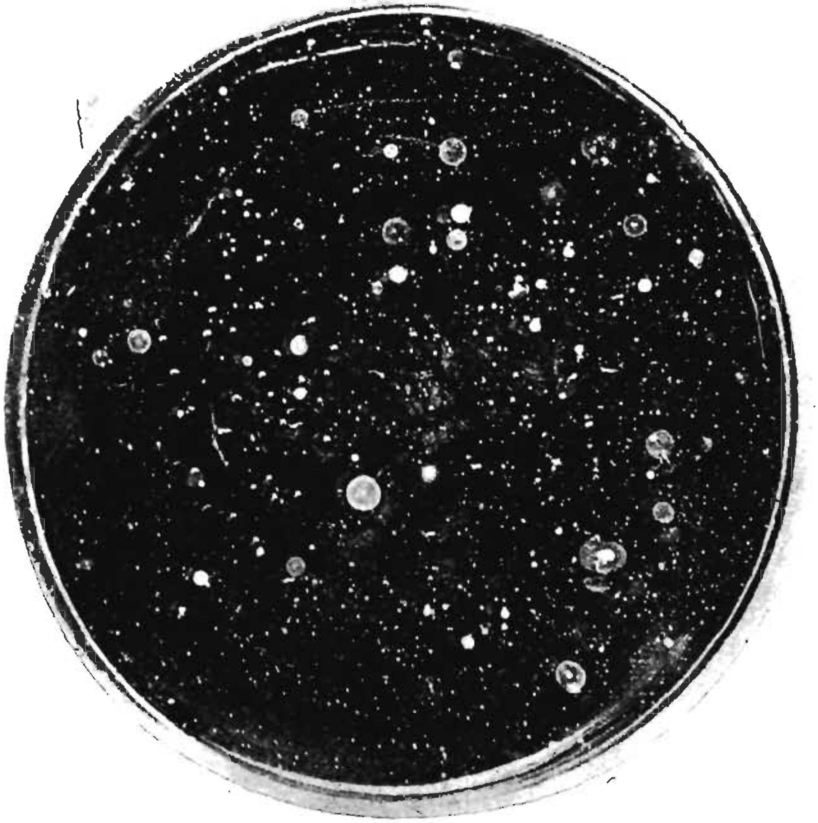


Fig. 65.—Typical Plate Culture on Gelatin of Soak Water Used for Softening Dried Sheep Skins.

All these may be classed as putrefactive organisms that secrete a variety of enzymes, many of which act energetically on hide substance.

Fig. 65, taken from Wood's paper, shows a typical plate culture on gelatin of a soak water used for softening dried sheep skins, in which no chemicals were used. The development of the colonies had to be stopped by the application of formaline vapor before many of the species had time to develop; otherwise the whole plate would have been liquefied.

Rideal and Orchard[6] examined the action of B. fluorescens liquefaciens on gelatin to which had been added 10 per cent of Pasteur's solution to serve as nutrient medium. The gelatin was completely liquefied in three and one-half days. It was shown that the liquefaction of the gelatin was due to an enzyme secreted by the bacteria. The liquefied gelatin was alkaline and had a slight odor suggesting putrefaction, but contained no hydrogen sulfide. A notable feature was the small amount of ammonia and volatile bases produced; only 0.2 gram of ammonia per 100 cubic centimeters was produced even after 16 days' incubation.

In bacterial action of a certain type, one of the first effects to be noticed is the loosening of the hair, a condition known to the trade as hair-slippiness. Either the bacteria, or the enzymes which they secrete, act upon the soft epithelial cells of the Malpighian layer of the epidermis, liquefying them and thus effecting a separation of the whole of the epidermis and hair from the rest of the skin. This action alone is not harmful, but the bacteria develop rapidly and soon begin to attack the fibers in the grain surface and the skin is permanently injured. This effect shows itself in the finished leather in the form of dull spots, or what is known as pitted grain. In some cases the bacteria attack the heavier collagen fibers without injuring the fibers of the grain surface. When the bacteria attack the proteins of the thermostat layer, they weaken the connection between the fibers of the grain surface and those of the reticular layer; in the finished leather the grain surface then tends to peel off and its looseness of connection with the main body of the skin gives it the appearance known as pipy grain.

Chemists not familiar with the chemical composition of fresh skin sometimes fall into the error of assuming that the presence of nitrogenous matter in a used soak liquor indicates that the collagen fibers have been attacked. One of the objects of soaking skins is to remove the soluble proteins so that they will not be carried forward to contaminate the liquors used to loosen the hair.

Bacteria may become lodged just under the grain surface of the skin and resist the action of the various liquors through which the skin passes. They then become the source of many most annoying troubles. They may produce dull spots or stains or hydrolyze the fats used later to soften the leather. Hydrolyzed and oxidized fats are the common sources of spews appearing on the surface of finished leather.

In the use of what is known as the putrid soak, bacteria are put to work by being made to assist in the softening of dried hides. But this method is not only an obnoxious one, but one so difficult to control that some damage very often accompanies the softening action. The method is seldom used in modern countries, but in some parts of India dried skins are softened by soaking them in putrid pools of liquor containing all kinds of tannery refuse.

In most tanneries, no attempt is made to utilize the bacteria of the soak waters. On the contrary all practical means available are used

[6] *Analyst*, Oct., 1897.

to prevent bacterial action in the soaking operation. In a study of the effect of hydrogen-ion concentration upon the activities of putrefactive bacteria, the author has found that they are most active between the pH values 5.5 and 6.0. This probably explains the value of using alkaline soak waters; the liquefaction of skin by bacteria at a pH value of 5.5 is usually greatly retarded or even completely checked by raising the pH value to 12. A similar effect is observed by lowering the pH value to about 3 by the addition of acid.

Procter[7] has pointed out the advantages of using sulfurous acid in the soak waters. It assists in the absorption of water by the skin and at the same time prevents bacterial action. He found that no putrefaction takes place, even if the skins are later retained for a considerable time in water, and the acid has little or no solvent effect on the collagen fibers, whose strength is well preserved.

Alkalies are about equally effective as acids both in the softening of dried skins and in checking bacterial action and are generally preferred because they assist rather than retard the action of the lime liquors in loosening the hair.

Aside from the use of acids and alkalies, the chief precaution taken against bacterial action in the soaks is the use of plenty of clean, cold water. If the temperature of the water is not allowed to rise above 10° C. and plenty of clean water is used, the skins are not likely to suffer any serious damage from the soaking operation itself.

[7] Principles of Leather Manufacture, Second Edition (1922), 161.

Chapter 6.

Unhairing and Scudding.

After the skins have been trimmed, cleansed, freed from adipose tissue and soluble matter, and have again become soft through absorption of their normal water content, they are ready for the series of operations involved in the removal of the epidermal system. It will be recalled from Chapter 2 that this system includes the epidermis, hair, and the sebaceous and sudoriferous glands and differs from the true skin under it in origin, structure, method of growth, and chemical composition. The several parts of the epidermal system differ markedly in their resistance to chemical reagents and it is rather fortunate for the tanner that the part most readily digested is the portion of the Malpighian layer resting on the grain surface. When the epithelial cells of this layer are destroyed, the rest of the epidermis and the hair become completely separated from the true skin and can easily be removed mechanically.

Sweating.

What is probably the oldest method known for unhairing skins received the name *sweating* from the nature of the process in its more highly developed state. It consists of little more than the putrefaction of the cells of the Malpighian layer. Since it is only necessary to allow a fresh skin to remain for a day or two in a warm, damp place to cause a loosening of the hair, the method was probably discovered very early in the history of the human race. It is not improbable that the accidental discovery of this action first revealed to the ancients the advantages of unhaired skins for certain purposes.

Because of the danger of serious damage to the skins in the sweat chambers, unless the process was very carefully watched and controlled, it ceased to be popular for the best grades of skins after safer methods of unhairing were devised. It is still in use in some tanneries for the lower grades of skins, such as the cheaper classes of dried hides and sheep skins where the wool is valued more highly than the skin.

The skins are generally hung from beams in a closed room in which the air is kept warm and humid. The temperature, humidity, and ventilation must be carefully controlled. During the process a considerable quantity of ammonia is evolved and this assists in the unhairing action. Just as soon as the hair slips easily, the skins are removed from the sweat chamber and dumped into saturated lime water. The lime water serves to retard further bacterial action and to cause the skins

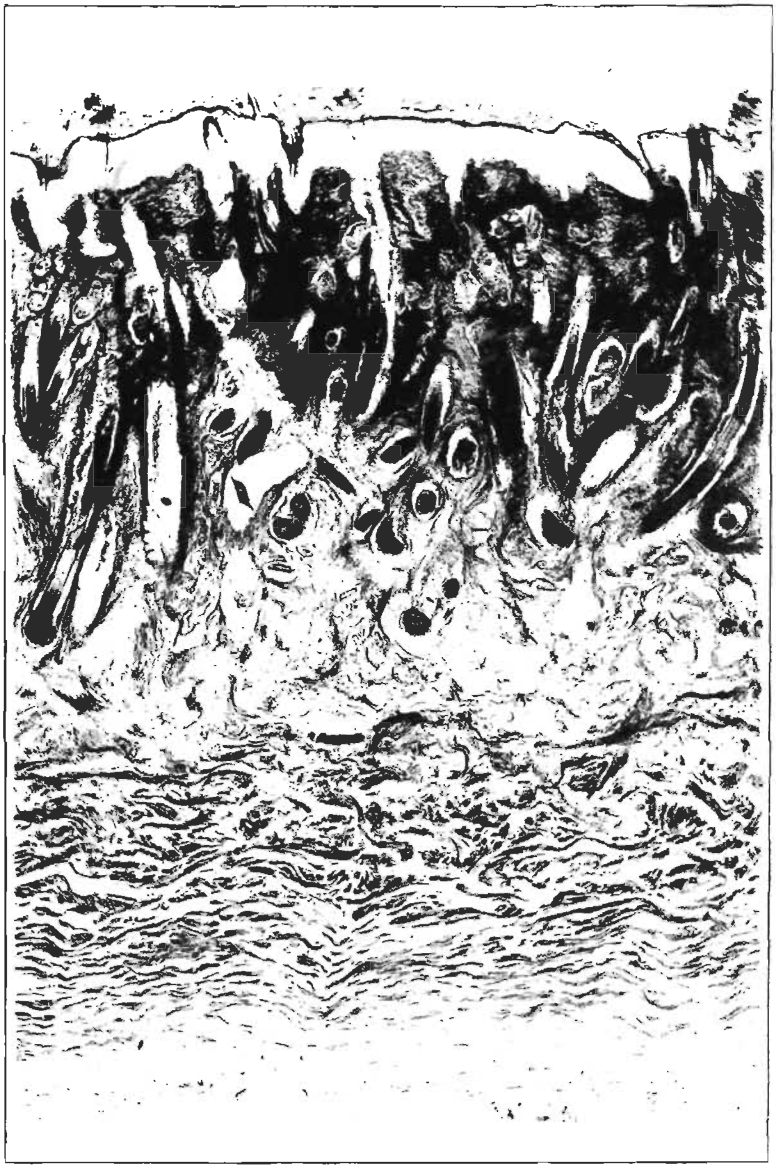


Fig. 66.—Vertical Section of Sheep Skin.
(After 42 hours in sweat chamber.)

Location: butt.
Thickness of section: 20 μ.
Stains: Van Heurck's logwood, Daub's bismarck brown.

Eyepiece: none.
Objective: 16-mm.
Wratten filter: H-blue green
Magnification: 45 diameters.

Fig. 67.—Vertical Section of Thermostat Layer of Sheep Skin.
(After 42 hours in sweat chamber.)

Location: butt.
Thickness of section: 20 μ.
Stains: Van Heurck's logwood, Daub's bismarck brown.

Eyepiece: 5X.
Objective: 16 mm.
Wratten filter: H blue green.
Magnification: 135 diameters.

to swell somewhat by absorption of water; the skins upon coming from the sweat chamber are in a very flaccid and slimy condition.

Wilson and Daub[1] recently made a study of the sweating process under the microscope. Pieces of fresh sheep skin were kept in a closed receptacle having an atmosphere saturated with water vapor at 38° C. At frequent intervals strips of skin were removed for sectioning and examining under the microscope. At the end of 42 hours, the wool could be rubbed off with ease and the skin had apparently suffered no damage. The odor of ammonia in the receptacle after the first day was very pronounced.

The first sign of action visible under the microscope was the separation of the cells of the Malpighian layer from one another and from the surface of the derma. This action gradually spread to the outermost layers of cells of the sebaceous and sudoriferous glands. On the second day the action had proceeded so far that the epidermis, glands and wool were completely separated from the derma and many of the epithelial cells had completely disintegrated. A section of the skin after being in the sweat chamber for 42 hours is shown in Fig. 66. The upper portion of the section is shown in Fig. 67 at a much higher magnification.

It will be noted that the corneous layer is still intact, but the Malpighian layer has almost completely disintegrated, the linings of the hair follicles are broken up, and the glands have all been loosened and separated from the derma. Fig. 66 should be compared with Fig. 28, which represents a section from the same skin fixed in Erlicki's fluid within an hour after the death of the animal.

In practice, the systematic cleaning of the sweat chambers is necessary in order to prevent the increase of undesirable organisms that may be carried in from time to time. Hampshire[2] investigated the cause of a pitting, or liquefaction in spots, of the grain and flesh surfaces of sheep skins, a damage known to the trade as *run pelts*. He found that the pitting was caused by several species of wormlike organisms belonging to the family *Nemathelminthes* and growing to a length of about one millimeter. Apparently they are killed by simple drying. They were found in great numbers in the sweat chambers, but not on skins which had not yet entered the chambers. In laboratory experiments, they produced a pitting of the skin in the presence of a small amount of ammonia, such as is always present in the sweat chambers. It was found that uniform slipping of the wool could be produced by incubating the skin in a clean vessel which excluded all organisms other than those present on the incoming skin, and skin treated in this way was free from pitting. It would seem that the danger of run pelts can be completely avoided by making certain of the cleanliness of the sweat chamber before the skins enter.

Upon coming from the sweat chamber, the skins are usually put

[1] The Mechanism of Unhairing. J. A. Wilson and Guido Daub. Presented before the Leather Division at the 64th meeting of the American Chemical Society. Publication of photomicrographs reserved for this book.

[2] Causes of Run Pelts in the Sweating Process. P. Hampshire. *J. Soc. Leather Trades Chem.* 5 (1921), 20.

into saturated lime water and left there for a few hours or over night. Although this treatment is not essential and is sometimes omitted, it has the advantage of decreasing the danger of damage to the skins through putrefaction. The next step is the actual removal of the hair and epidermis. In modern practice, this is accomplished by means of an unhairing machine in which the skin is backed by a rubber slab and blunt knife blades pass over the hair side, under low pressure, rubbing

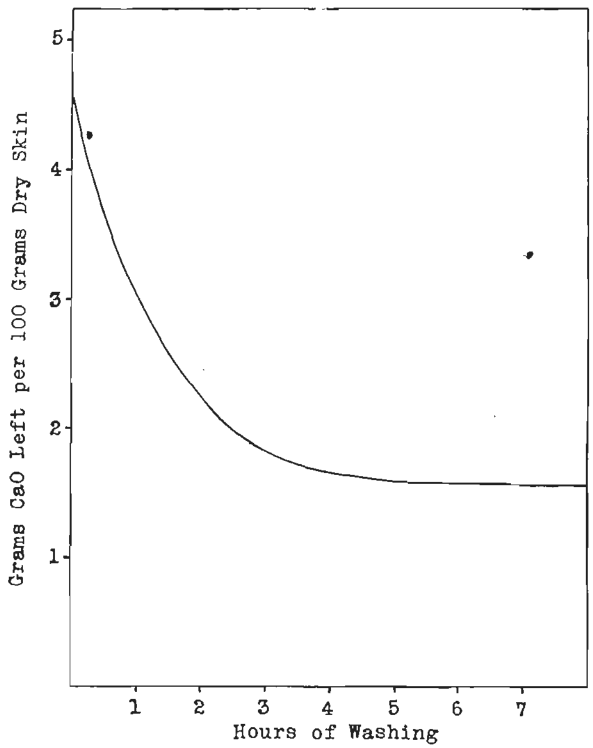


FIG. 68.—Removal of lime from unhaired skin by washing.

off the hair and epidermis. Often the blades are set in rollers which rotate as they pass over the skin.

The skin is then placed over a *beam* and *scudded*. The beam, from which the beamhouse derived its name, is a convex wooden slab sloping upward from the floor, at an angle of about 30°, to a point about three feet higher, which gives it a length of about six feet. The *beamster*, leaning over the beam, pushes a specially designed, two-handled knife over the skin downward and to left and right, forcing the remnants of the glands, lime soaps, dirt, and any remaining hairs out of the hair follicles and pores. This operation is known as scudding.

Goat skins can be scudded satisfactorily by machine after the bating

operation, but the author knows of no machine that can replace a good beamster for scudding calf skins after liming. Scudding can usually be done better by hand than by machine because the hair follicles slope in many different directions. If the knife stroke is made in the direction of the hair, from root to tip, the dirt in the follicles is easily squeezed out, whereas there is a tendency for it to be trapped by a stroke in the opposite direction. There is a sufficient degree of transparency to a limed skin to enable the beamster to see the dirt and pigment in the follicles and he directs his knife first one way and then another until the skin appears clean. He is also on the lookout for fine hairs not removed by the machine. The bulb of a new hair is as deeply seated as that of an old one, but there may not be enough of the new hair protruding above the surface of the skin to be gripped by the knives of the unhairing machine.

After the scudding operation, the skins are washed thoroughly to remove as much lime as possible. This washing is of considerable importance because any great excess of lime carried forward interferes with the later processes. It is customary to wash the skins in a revolving drum through which fresh water is continually passing. Wood[3] followed the removal of lime during washing and showed that little is to be gained by continuing the washing for more than two hours. The tendency, however, is to wash the skins for a shorter time than this and to take care of the residual lime by other means. Fig. 68 shows the extent of lime removal with time during a typical washing operation. The lime left in the skins appears to approach a limiting value, due to the lime which has carbonated as well as that in chemical combination with the skin.

Liming.

The commonest method in use today for effecting the separation of the epidermal system from the true skin is also one of ancient origin and is known as liming from the fact that saturated lime water is used. Formerly a lime liquor was prepared simply by filling a vat with water and adding calcium hydroxide greatly in excess of saturation. The skins, after soaking, were put into this liquor and allowed to remain there until the hair and epidermis had become so loosened that they could be rubbed off with very little pressure. Often the skins were removed each day and fresh lime added in order to hasten the action. But with a fresh lime liquor it usually required weeks for the skins to get into a state where the hair would slip easily. It was discovered that less time was required for each succeeding lot of skins passing through a given liquor. The longer a liquor was used the more it became charged with ammonia, other protein decomposition products, bacteria, and enzymes, all of which assisted in loosening the hair. The older liquors, however, attacked the collagen fibers to a greater extent and also produced less swelling of the skin proteins than fresh liquors.

[3] The Puering, Bating and Drenching of Skins. J. T. Wood. E. & F. N. Spon, London (1912).

As more was learned of the action of lime liquors, it became customary to employ a series of liquors for each lot of skins. The skins were put first into the oldest liquor in order to start the loosening of the hair. Each day they were moved into a fresher liquor and finally into one quite fresh. This system is still in use in some tanneries, but the modern tendency is toward quicker methods.

When lime alone was used in making lime liquors, it usually required from one to three weeks to cause the hair to slip easily, during which time a considerable amount of collagen became hydrolyzed, especially in old liquors or in liquors not kept completely saturated with lime at all times. Bacteria are very sensitive to changes in pH value and many proteolytic bacteria present in lime liquors which are comparatively inactive at a pH value of 12.5, that of an ordinary lime liquor, become very active as the pH value falls to lower values. In order to guard against the danger of incomplete saturation of the liquors with lime, mechanical agitators have been devised, one of the simplest being a paddle wheel set in the vat. By keeping the undissolved lime continually stirred up, the solution is kept almost at the saturation point.

With increasing demand for speed of operation and conservation of the skin collagen, *sharpening agents* have come into wide use, the principal ones being arsenic sulfide, sodium sulfide, and sodium hydroxide. The judicious use of these materials, in conjunction with lime, has reduced the time required to unhair skins from weeks to as many days. More attention was paid also to temperature. In some of the old tanneries not equipped to heat the liquors, a much longer time had to be allowed for unhairing in winter than in summer. It is now customary to maintain a uniform temperature of from 20° to 25° C. the year round.

Arsenic disulfide was one of the first sharpening agents to be employed. It was mixed with the lime before slaking in the proportion of about one part of sulfide to twenty-five parts of lime and from this mixture a liquor was made of such concentration that the hair would not be damaged, but would slip easily in two or three days. Sodium sulfide is now used more commonly than arsenic, being cheaper and somewhat more effective in loosening the hair. It is used at about 0.01 molar concentration in a solution kept saturated with lime.

The action of a lime liquor sharpened with sodium sulfide upon a calf skin is illustrated in Fig. 69. A fresh calf skin was put into a solution containing 0.7 gram of Na_2S per liter and calcium hydroxide well in excess of saturation. The liquor was agitated frequently and kept at a temperature of 25° C. Strips of the skin were examined at intervals as in the study of the sweating process. The skin from the sweating process was in a soft, flaccid condition, while that from the lime liquor was plump and rubbery, but the fate of the epithelial cells of the Malpighian layer was the same in both cases. Sections of specimens taken at intervals showed these cells slowly disintegrating and leaving the corneous layer, hairs, and glands separated from the derma. Fig. 69 shows a section taken after the skin had been in the lime liquor for 48 hours. Part of the upper region of the section is shown at

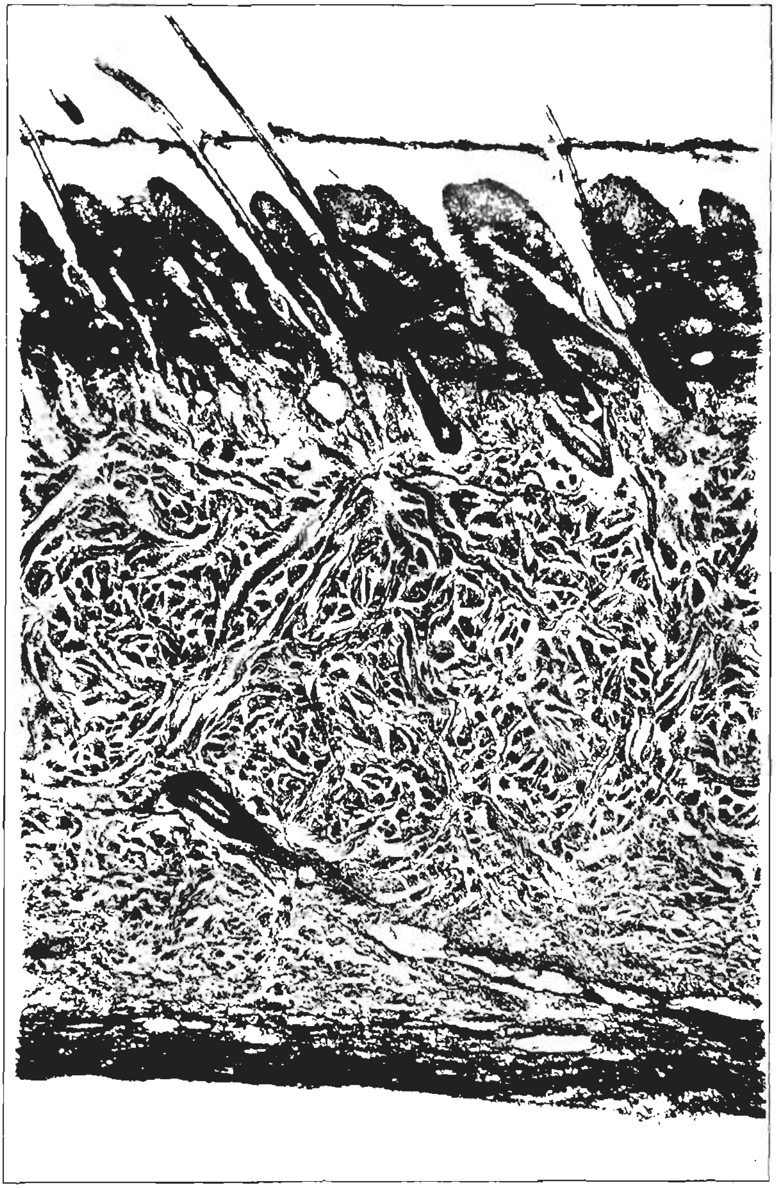


Fig. 69.—Vertical Section of Calf Skin.
(After 48 hours in lime liquor.)

Location: butt.
Thickness of section: 40 μ.
Stains: Weigert's resorcin fuchsin and picro-red.
Eyepiece: none.
Objective: 32-mm.
Wratten filters: B-green; E-orange.
Magnification: 25 diameters.

Fig. 70.—Vertical Section of Thermostat Layer of Calf Skin.
(After 48 hours in lime liquor.)

Location: butt.
Thickness of section: 40 μ.
Stains: Weigert's resorcin-fuchsin and picro-red.

Eyepiece: 5X.
Objective: 16-mm.
Wratten filters: B-green; E-orange.
Magnification: 135 diameters.

higher magnification in Fig. 70. The section is from the same skin as that shown in Fig. 18, which represents the fresh skin as it existed in life.

The lime has completely destroyed the Malpighian layer of the epidermis and the corneous layer appears as a nearly continuous line somewhat separated from the true skin. The epithelial cells of the hair follicles have been completely broken up leaving the hair, with adhering patches of corneous layer, free to be swept out by the action of the unhairing machine. The sudoriferous glands have disintegrated, leaving empty spaces, and the sebaceous glands may be seen lodged in pockets opening into the hair follicles. The erector pili muscles are still intact and can be seen runing upward to the left from the region of the hair bulbs. In the thermostat layer, as well as in the deepest layer of the skin, the elastin fibers appear as fine, black threads. These fibers do not appear prominently in Fig. 18 because this section was stained with the object of showing greater detail in other parts.

Although the hair loosening operation can be effected easily in a single liquor acting for two or three days, some tanners still prefer to use a series of liquors, claiming that they get a result better adapted for the particular kinds of leather they desire to make. They lessen the extra amount of labor involved in handling the skins by a system of reeling from vat to vat. The skins are all hooked or tied together, the head of one to the tail of another, and the whole lot is passed over a reel from one vat to another, the last skin in being the first to come out. The skins are put first into the oldest liquor and then reeled into a fresher liquor each day until ready to be unhaired.

Plumping and Falling.

When animal skin is immersed in dilute solutions of acid or alkali, the protein matter swells by absorbing some of the solution, but the effect to a casual observer is not so much one of swelling as of increased resiliency of the skin, due to its fibrous structure. The collagen fibers, in swelling, tend to fill up the interstices between them and the full increase in volume of the protein matter is not evident from the appearance of the skin. A skin in which the fibers are not swollen may contain practically as much water as one whose fibers are swollen, as in lime water, but the bulk of the water in the first skin is held only loosely *between* the fibers and may be squeezed out by the application of slight pressure, whereas that in the second is present *within* the substance of the fibers, like the water absorbed by a solid block of gelatin jelly, and cannot be removed, except by the application of enormous forces. During the swelling of the protein matter, the tanner observes in the skin an increasing resistance to compression, to which he has given the name *plumping*, the term *falling* indicating the reverse action.

Wood, Sand and Law [4] devised an apparatus for determining when

[4] The Quantitative Determination of the Falling of Skin in the Puering or Bating Process. J. T. Wood, H. J. S. Sand and D. J. Law. *J. Soc. Chem. Ind.* 31 (1912), 210 and 32 (1913), 398.

a skin had become completely fallen during the bating process which consisted of a sensitive thickness gauge in which the pressure exerted upon 1 square centimeter of skin could be varied by means of weights. The point of complete falling of a skin was taken as that at which no recovery in thickness of the skin took place upon removing the weights. The apparatus was also used to measure the apparent modulus of elasticity of the skin and this was considered to be a measure of the degree of plumping.

This method suggested to Wilson and Gallun[5] another which is more suitable for certain purposes. Their apparatus consisted of a Randall and Stickney thickness gauge[5a] with a flat, metal base upon which a small piece of skin could be placed, and a plunger, having a circular base 1 square centimeter in area, capable of pressing on the surface of the skin under constant pressure. The apparent thickness of the skin, as shown on the dial of the instrument, being determined by the position of the plunger, decreased with time as the plunger caused an increasing degree of compression. For this reason and in order to get comparative readings, all gauge readings were taken a fixed length of time after dropping the plunger onto the skin. In order to measure the degree of plumping of skin in a given liquor under fixed conditions, they first measured the resistance to compression of a small piece of skin under standard conditions. This same piece of skin was then subjected to the conditions of the test and its resistance to compression measured again. In each case the gauge reading was taken as a measure of the resistance to compression. The ratio of the final to the initial gauge reading is a measure of the degree of plumping of the skin. Their measurements of the degree of plumping of calf skin as a function of pH value are given in Chapter 9.

If a skin in the alkaline state is plumped or swollen excessively, it suffers permanent distortion and the value of the final leather is lowered. Some knowledge of the degree of plumping of skin in liquors used for unhairing is therefore much to be desired.

Atkin[6] was able to reason from the work of Procter, Wilson, and Loeb, which was discussed in Chapter 5 in connection with the swelling of protein jellies, that arsenic disulfide is preferable to sodium sulfide for certain kinds of skin where fineness of grain surface is of paramount importance in the finished leather. Loeb showed that diacid bases produce a maximum swelling of gelatin jelly only half as great as that produced by monacid bases. Atkin confirmed this for the swelling of hide powder and showed that the weak base ammonium hydroxide produces as much swelling as sodium hydroxide at the same pH values. When arsenic disulfide is slaked with lime and used in a fresh liquor, the solute consists only of calcium hydroxide, calcium sulfhydrate, and calcium sulfarsenite. But when sodium sulfide is used as the sharpening agent for a lime liquor, sodium hydroxide and sodium

[5] Direct Determination of the Plumping Power of Tan Liquors. J. A. Wilson and A. F. Gallun, Jr. *Ind. Eng. Chem.* 15 (1923), 376.

[5a] Made by Randall and Stickney, Waltham, Mass.

[6] Notes on the Chemistry of Lime Liquors Used in the Tannery. W. R. Atkin, *J. Ind. Eng. Chem.* 14 (1922), 412.

sulfhydrate are present. It would therefore be expected that the use of sodium sulfide would result in a greater plumping of the skin than the use of arsenic sulfide, which gives a liquor containing only divalent cations. In actual practice, when arsenic sulfide is used to sharpen lime liquors for the unhairing of goat skins in the manufacture of glazed kid leather, the final leather has a smoother and silkier grain surface than when sodium sulfide is used in the lime liquors.

It might be inferred from this that it is preferable to use arsenic sulfide for all kinds of skin where smoothness of grain is desired, but this is not necessarily so. All skins are not equally sensitive to injury through plumping. What may prove to be excessive plumping for goat skins may not have any deleterious effect at all on a calf skin and one type of calf skin might be more resistant to permanent distortion than another. The greater speed of action and lower cost of sodium sulfide makes its use preferable in all cases where it does no harm to the skins.

It sometimes happens that a skin can be unhaired less readily the more it is plumped. This seems to be due to the overlapping scales of the hair, which open upward as shown in Fig. 6. When the skin is put into a liquor in which it swells considerably, the hair becomes tightly pinched by the skin and at the same time the scales become distended, their ends wedging themselves into the sides of the follicles in such manner as to resist any attempt to pull the hair out. If the fine hairs are not removed from a skin while it is still in the alkaline condition, but are allowed to remain in place until after the tanning operation, they again become firmly fixed in place, apparently because of the distention of the hair scales and the permanent plumping of the skin produced by the tannage.

Fresh vs. Mellow Lime Liquors.

A much used lime liquor, charged with decomposition products of the skin, bacteria and enzymes, is usually referred to as *mellow*. Where unsharpened lime liquors are used, a mellow liquor causes a much more rapid loosening of the hair and much less plumping of the skin than a fresh liquor. This difference is not due to any difference in hydroxide-ion concentration for Wood and Law [7] have shown that a mellow lime liquor has a pH value practically the same as that of pure saturated lime water. They found also that the pH value is but little affected by the addition of small quantities of sodium sulfide and this has been confirmed in the author's laboratories. The decrease in plumping power of a lime liquor with use may be ascribed to the calcium salts formed, which tend to repress the swelling of proteins by calcium hydroxide. But the increasing power to loosen the hair must be attributed to the protein decomposition products, bacteria, enzymes, or the lesser swelling of the skin at the same pH value, or possibly to a combination of all four factors.

Wood and Law regard the growth of bacteria in lime liquors as the principal factor in the production of mellowness. They examined

[7] Light Leather Liming Control. J. T. Wood and D. J. Law. *Collegium* (1912), 121.

an old lime liquor in which skins had been worked for 3 to 4 weeks and obtained a count of 50,000 bacteria per cubic centimeter of a type capable of developing in ordinary nutrient gelatin containing ammonia. They identified *Micrococcus flavus liquefaciens* and *B. prodigiosus,* both of which are known to produce proteolytic enzymes. The bacteria found on the roots of wool from the sweating process were found to be capable of growing in a liquid as alkaline as 0.05 normal. These appear to be similar to the bacteria commonly present in mellow lime liquors and Wood considers it highly probable that the unhairing action both in the sweat chamber and in mellow lime liquors is due to the same bacteria, not necessarily belonging to a single species.

Stiasny[8] also showed that bacteria play an important rôle in old lime liquors. An untreated mellow lime liquor caused a loosening of the hair of calf skin in 24 hours, but in a test where chloroform was added to the same liquor to check bacterial action the liquor was not able to cause any loosening of the hair in 3 days. A portion of the untreated liquor was freed from ammonia by heating to 60° C. and passing carbon dioxide-free air through it for 4 hours. It then showed an unhairing power as great as before, but a lesser solvent action on the hide substance, indicating that the unhairing action is due to bacterial action rather than to the ammonia ordinarily present in mellow liquors.

Since sterile lime water appears to have but little unhairing action on skins, it was long thought that bacteria were necessary for this action, where no sharpening agent was employed. But Schlichte[9] found that skin previously sterilized by the Seymour-Jones process, with mercuric chloride and formic acid, could be unhaired easily after two weeks of contact with saturated lime water under sterile conditions. Wood and Law,[10] however, pointed out that the action may have been influenced by the previous swelling of the skin in the sterilizing solution. This is intelligible from the viewpoint of Stiasny,[11] who regards proteins as peptones held together relatively loosely by means of secondary valency forces. The peptones are considered to be built up of peptides held together by forces of primary valence. He assumes that the swelling of a protein jelly causes a diminution in the forces holding the peptones together. On this basis, the swollen protein, or one in which the bonds between the peptones had been weakened through previous swelling, would be attacked by hydrolyzing agents much more readily than the unswollen protein. In support of this view, he finds that collagen is attacked by trypsin very much more rapidly when swollen by potassium thiocyanate or iodide solutions and that the action then goes only to the peptone stage.

It was suggested by the author[12] that barium and calcium hydroxides

[8] The Nature of the Liming Process. E. Stiasny. *Gerber* (1906); English translation, *J. Soc. Leather Trades Chem.* 3 (1919), 129.

[9] A Study of the Changes in Skins during Their Conversion into Leather. A. A. Schlichte. *J. Am. Leather Chem. Assoc.* 10 (1915), 526 and 585.

[10] Note on the Action of Lime in the Unhairing Process. J. T. Wood and D. J. Law. *J. Soc. Chem. Ind.* 35 (1916), 585.

[11] Some Modern Problems in Leather Chemistry. E. Stiasny. *Science* 57 (1923), 483.

[12] Theories of Leather Chemistry. J. A. Wilson. *J. Am. Leather Chem. Assoc.* 12 (1917), 108.

hydrolyze proteins to a lesser extent than the hydroxides of sodium or ammonium because of the higher valency of the cations. The swelling of proteins in alkaline solution is due to the pull of the cations of the protein salt, which tend to diffuse from the region of high concentration of ions in the jelly to the region of lower concentration in the surrounding solution. If this pull is sufficiently great, we might reasonably expect a breaking up of the units making up the protein jelly. A sodium or ammonium ion exerts its entire pull upon a single unit, whereas the pull of a divalent cation is divided between two units, making the tendency towards decomposing the protein only half as great. This valency effect, however, is not the only one playing a part in sterile unhairing liquors because the mere replacement of half of the hydroxide ions of lime water by sulfhydrate ions is sufficient to cause a very marked increase in the rate of unhairing. Wood and Law suggested that Schlichte's observation of the unhairing power of sterile lime water is further complicated by the formation of sulfur compounds by the action of lime on the easily dissolved sulfur of the hair. Such compounds are capable of loosening the hair.

Unhairing by Means of Other Alkalies.

Pure solutions of sodium hydroxide and sodium sulfide quickly destroy the hair and epidermis when sufficiently concentrated. A 2-per cent solution of Na_2S at 25° C. will dissolve the hair and epidermis from the surface of a calf skin in about 2 hours, during which time only a comparatively small amount of collagen is destroyed. This treatment has been applied with considerable success to heavy hides, especially those which had previously been dried, and was a great help in speeding up the production of army leathers during the war. The hides were put into the sulfide solution, which was agitated by means of a paddle wheel. After several hours the hides were transferred to a solution of sodium bicarbonate or calcium chloride in order to stop the caustic action of the sodium sulfide. They were then washed and were ready for bating or tanning. The hair was completely dissolved from the surface of the hides in the sulfide liquor, but the action was so rapid that they had to be removed before the sulfide had diffused into them to the depth of the hair bulbs. As a result, the hair bulbs were usually left in the hides intact, as could be shown by examining sections under the microscope, but this apparently did not lower the value of the leather in any way.

With this method of unhairing, it was found economical to use the same liquor for a number of consecutive lots of skins, adding just enough fresh sodium sulfide each time to maintain the necessary concentration. The liquors soon became heavily charged with protein decomposition products which are soluble in alkaline solution, but are precipitated by rendering the solution faintly acid. Kadish and

Kadish[13] made use of this fact in a scheme for recovering this nitrogenous matter as fertilizer. The waste liquors were run into a mixing chamber where they were reacted upon by sulfuric, sulfurous, or other acid. The precipitated nitrogenous matter was separated from the mother liquor and the hydrogen sulfide was recovered separately in such manner as to make the entire operation continuous.

Using sodium hydroxide instead of the sulfide, a similar unhairing action is obtained, but the skin becomes much more swollen and plumped. For the finer grades of light skins, where a smooth grain surface is required, neither sodium hydroxide nor sulfide solutions can be used alone because of the rough grain resulting from the excessive plumping.

It is not an uncommon practice in dewooling sheep skins to paint them on the flesh side with a paste made of a mixture of lime and sodium sulfide. The skins are then folded, wool side out, and left until the sulfide has diffused into the skins as far as the hair bulbs. When these are destroyed, the wool can be pulled or brushed out. As a rule, the skins are thrown over a beam and the wool is worked off by a beamster. The skins are then limed, washed, bated, and pickled, in which condition they may be kept until required for tanning. Sometimes the paste is made from lime and arsenic sulfide.

Solutions of ammonia in twice-molar concentration have a very marked unhairing action on fresh skins. The author found that fresh calf skins could be unhaired quite satisfactorily after only two hours' immersion in such a solution. The skin swells but very little and the grain surface is left remarkably smooth and silky. If the skin is left in the solution longer than is necessary, however, there is danger of it suffering damage because of the powerful action of the ammonia on the collagen fibers. Since the unhairing powers of ammonia have long been known, it has often been wondered why its use has not become widespread. In an investigation, the author found that it could not be relied upon for unhairing the ordinary run of skins in commerce because its action is influenced by the previous treatment of the skin. On some skins, the ammonia would loosen the hair only in patches. In one experiment, a piece of fresh calf skin was cut into two pieces. One was put directly into twice-molar ammonia solution and the hair was loosened quite satisfactorily in two hours. The other was soaked in molar acetic acid for an hour, washed, neutralized with ammonia, and then put into the twice-normal ammonia solution. But there was no appreciable loosening of the hair after several hours.

Stiasny[14] studied the effect of adding different salts upon the unhairing action of ammonia. He used a series of liquors each consisting of half-normal ammonia and 0.07 normal chloride of sodium, calcium, barium, or zinc. One liquor contained ammonia alone. A piece of fresh calf skin was put into each. After 2 days the piece in am-

[13] V. H. Kadish, U. S. patent 1,269,189 (1918); V. H. and H. L. Kadish, U. S. patent 1,298,960 (1919).

[14] The Nature of the Liming Process, *loc. cit.*

monia alone had increased in weight 65.5 per cent, the one in the solution containing sodium chloride 45.8 per cent, in calcium chloride 14.9 per cent, in barium chloride 19.8 per cent, and in the solution containing zinc chloride 31.4 per cent. The hair was loosened in the solution of ammonia alone and in the one containing sodium chloride, but not in the others. Atkin[15] has pointed out that the difference in repression of swelling by the different salts may be attributed to the valency of the cation. It is, of course, evident that the difference in unhairing action may be explained in the same way. Stiasny, however, looked upon the difference in action as due to the formation of complexes between the ammonia and the divalent cations, giving salts of the type $Ca(NH_3)_8Cl_2$.

Unhairing by Means of Acids.

In 1916, Mr. J. T. Wood sent the author a piece of calf skin which had been sterilized by the Seymour-Jones process. The formic acid had caused a loosening of the hair, which Mr. Wood says was marked in 8 days. Thuau[16] and Nihoul[17] had previously shown that sulfurous acid will cause a loosening of the hair of skins, if used in solutions that will prevent the swelling of the skin, as in the presence of salt. Marriott[18] found that salted hide could be unhaired by immersion in 0.25-per cent acetic acid solution for 9 days.

In no case was the hair loosening by means of acid as satisfactory as can be obtained in alkaline solution. The acid seems to attack only the deepest layer of the epithelial cells of the Malpighian layer, leaving most of the epidermis intact, to be removed with the hair. It seems doubtful that acid will ever replace alkaline solutions for unhairing.

Unhairing by Means of Pancreatin.

In 1913, Röhm[19] described a process for unhairing and bating skins in one operation, involving the use of an alkaline solution of pancreatin. Since then pancreatin has often been listed as an unhairing agent. In 1920, Hollander[20] described Röhm's process as having a number of advantages over the old system of liming and claimed that it depends entirely upon enzyme action for unhairing. According to his description, the skins are first soaked for 1 day in dilute sodium hydroxide solution and then transferred to a dilute solution of sodium bicarbonate to which the enzyme is added after the swelling due to the alkali has been counteracted. Twenty-four hours later the hair is completely loosened and can be rubbed off.

Wilson and Gallun[21] investigated this method with the object of

[15] Notes on the Chemistry of Lime Liquors Used in the Tannery. *loc. cit.*
[16] Unhairing with Sulfurous Acid. U. J. Thuau. *Collegium* (1908), 362.
[17] Unhairing with Sulfurous Acid. E. Nihoul. *Bourse aux Cuirs de Liège* (1908), 8.
[18] Acid Unhairing. R. H. Marriott. *J. Soc. Leather Trades Chem.* 5 (1921), 2.
[19] A New System of Liming. O. Röhm. *Collegium* (1913), 374; *J. Am. Leather Chem. Assoc.* 8 (1913), 408.
[20] Unhairing Hides and Skins by Enzyme Action. C. S. Hollander. *J. Am. Leather Chem. Assoc.* 15 (1920), 477.
[21] Pancreatin as an Unhairing Agent. J. A. Wilson and A. F. Gallun, Jr. *Ind. Eng. Chem.* 15 (1923), 267.

determining the specific rôle played by the enzyme. They made a preliminary examination by soaking pieces of thoroughly cleansed calf skin in 0.05 molar sodium hydroxide solution for 1 day, replacing the solution next day by 0.1 molar sodium bicarbonate solution, and 5 hours later transferring the pieces to a solution made by diluting 18 cubic centimeters of molar sodium hydroxide, 2.8 grams of monosodium phosphate, and 1 gram of U.S.P. pancreatin to 1 liter. The pH value of the solution was found to be 7.52 at 25° C., lying well within the range of optimum activity of this enzyme. Two experiments were run at a temperature of 25° C., but in one the solutions were left exposed to air, as would be the case in practice, while in the other they were covered with a layer of toluene to check bacterial action. After the pieces had been in the enzyme solutions for 24 hours, the hair of the pieces from the solutions exposed to air could be rubbed off with the greatest ease, leaving the grain surface clean and white, but that of the pieces from the solutions under toluene remained firmly fixed. This seemed to indicate that the unhairing action obtained at 25° was not due to the enzyme, but probably to proteolytic bacteria or their products.

Because of the doubt thus cast upon the rôle played by pancreatin in this method of unhairing, Wilson and Gallun carried the investigation further, paying particular attention to the action of pancreatin at 40° C., the temperature of its maximum activity. The studies were made upon pieces of fresh calf skin, about 5 x 3 inches, which had been thoroughly soaked and cleansed. Each experiment was carried out both at 25° and at 40° C. The action of the enzyme solution upon the skin in each test was compared with the action of a blank identical with the enzyme solution except for the fact that it contained no enzyme. This solution was prepared by diluting 18 cubic centimeters of molar sodium hydroxide solution and 2.8 grams of monosodium phosphate to 1 liter and all enzyme solutions were made by adding to it 1 gram of pancreatin per liter. The pH values did not vary more than 0.1 from the value 7.6 in any case. The enzyme solutions and blanks as well as solutions used for the pretreatment of the skin were all covered with a layer of toluene to check bacterial action. The results were checked on separate occasions with pieces of skin from different sources.

The effect of pancreatin upon skin not previously soaked in sodium hydroxide solution, or any other swelling agent, was studied first. After 24 hours of contact of skin and solution, little action was noticeable either at 25° or 40°, but after 48 hours the collagen fibers of the skin in the enzyme solution at 40° began to dissolve very rapidly, the action proceeding from the flesh side, but there was no indication of the hair becoming loosened. On the other hand, the skin in the blank at 40° and those at 25° in both blank and enzyme solution still remained but little affected. It was evident that pancreatin has a more powerful solvent action upon the collagen fibers than upon the epidermis of a skin not previously swollen with acid or alkali. The time factor involved in the destruction of the collagen fibers is in-

teresting. The action seemed to indicate that the fibers were coated with some material more resistant to tryptic digestion than the collagen beneath it. Possibly this supposed covering may be found to bear some relation to what Seymour-Jones[22] has called the fiber "sarcolemma."

In the next series of experiments, the pieces of skin were kept for 24 hours in 0.05 molar sodium hydroxide solution at 25° and 40° C., respectively. The solutions were then replaced by 0.1 molar sodium bicarbonate solutions of corresponding temperatures, and 5 hours later by the enzyme and blank solutions, in which the skins remained for 24 hours. The unhairing action in the enzyme solution at 40° was completely satisfactory, indicating that, at this temperature, pancreatin may be considered an unhairing agent for calf skin previously swollen in dilute sodium hydroxide solution. A very slight unhairing action was noticeable in the blank at 40°, evidently due to the previous treatment with alkali. No unhairing action could be detected in the blank or enzyme solution at 25°.

The preceding series of experiments was then repeated exactly, except that 0.05 molar hydrochloric acid solution was substituted for the alkali as the swelling agent. At 25° there was no visible unhairing action either in the blank or enzyme solution. In the hydrochloric acid solutions in the bath at 40°, the pieces of skin began to jelly; there was no further change in the piece transferred to the blank at 40°, but the piece put into the enzyme solution at 40° was quickly destroyed, the collagen passing into solution, leaving the epidermis and hair floating in the liquor. The opposite effects of acid and alkali upon the skin at 40° is interesting. 0.05 molar sodium hydroxide solution hydrolyzes the epidermis more rapidly than the collagen fibers, whereas 0.05 molar hydrochloric acid hydrolyzes collagen much more rapidly than it does the epidermis.

The experiment was repeated except for the fact that the pretreatment with hydrochloric acid was done at 25° and the digestion with pancreatin at 40°. After the skin had been in the pancreatin solution for 24 hours, the hair was completely loosened, showing that the effectiveness of pancreatin as an unhairing agent depends upon the previous swelling of the skin, but regardless of whether the swelling is caused by acid or alkali. The fact that pretreatment with sodium hydroxide in the experiment with alkalies was done at 40° did not seriously influence the result for, when another piece of skin was soaked in 0.05 molar sodium hydroxide solution at 25° for a day and then in the pancreatin solution at 40°, the unhairing action was entirely satisfactory.

Experiments dealing with the action of pancreatin upon skins previously treated with ammonia were carried out exactly like those of the sodium hydroxide series, except for the replacement of the 0.05 molar sodium hydroxide solution by 0.50 molar ammonium hydroxide solution. The hair was loosened to some extent by the

[22] Physiology of the Skin. Alfred Seymour-Jones. *J. Soc. Leather Trades Chem.* 2 (1918), 203.

pretreatment with ammonia, more at 40° than at 25°. After the pieces had been in the blank and enzyme solutions for 24 hours, they all showed some unhairing action, but in no case was it entirely satisfactory. The degree of action might be given a very rough rating by calling that in the enzyme solution at 40° 75 per cent, that in the blank at 40° 50 per cent, and that in both blank and enzyme solutions at 25° 25 per cent. Evidently the pretreatment of skin with ammonia, which is itself an unhairing agent, does not assist the unhairing action of pancreatin nearly so much as pretreatment with materials whose action is primarily to swell the skin.

Combined Bating and Unhairing by Means of Pancreatin.

Wilson and Gallun extended their investigation to an examination of the effect of the pancreatin upon the elastin fibers of the skin, the work of Wilson and Daub having indicated previously that the fundamental action of bating is the removal of elastin fibers from the skin. The work of Wilson and Daub will be described in the next chapter. Pieces of skin were taken from the various experiments after the pancreatin had acted upon them. These were imbedded, sectioned, stained, and mounted for examination, as described in Chapter 2.

When the pancreatin method of unhairing is used in practice, the liquors are left exposed to air. The experiments of Wilson and Gallun show that the hair loosening can then be effected at a temperature of 25° C., but that the action is apparently not due to enzyme, but rather to bacteria, since it is checked by covering the solutions with toluene. But, if pancreatin is not the active agent, we should expect the action not to be accompanied by elastin removal. Fig. 71 corroborates this view; where the hair loosening was effected by a pancreatin solution at 25°, exposed to air, the epidermis is disintegrated and the hair loosened, but the elastin fibers remain undissolved and show in the upper half of the picture as fine, black threads running nearly horizontally.

In the unhairing experiments where the skin from the enzyme solutions at 40° C. had not previously been swollen with acid or alkali, microscopic examination showed that all of the elastin had been dissolved away from the flesh side of the skin in 24 hours, but none from the region just under the epidermis. The hard corneous layer of the epidermis had apparently acted as a membrane impermeable to the enzyme. In the ordinary methods of unhairing, such as liming, the unhairing agent acts upon the cells of the Malpighian layer, which lie between the corneous layer and the derma. The impermeability of the corneous layer to the enzyme explains why the pancreatin did not attack the Malpighian layer and loosen the hair. In acid or alkaline solutions, the corneous layer swells considerably and is thereby rendered more permeable. It is also attacked by the enzyme, when in the swollen condition, as shown by the fact that no corneous layer could be found in the sections examined.

Fig. 71.—Vertical Section of Thermostat Layer of Calf Skin.
(After 1 day in 0.1-per cent pancreatin solution at 25° C.)

Location: butt.
Thickness of section: 30 μ.
Stains: Van Heurck's logwood, Daub's bismarck brown.

Eyepiece: 5X.
Objective: 8-mm.
Wratten filter: H-blue green.
Magnification: 170 diameters.

Fig. 72.—Vertical Section of Thermostat Layer of Calf Skin.
(After 1 day in 0.1-per cent pancreatin solution at 40° C.)

Location: butt.
Thickness of section: 30 μ.
Stains: Van Heurck's logwood, Daub's bismarck brown.

Eyepiece: 5X.
Objective: 8-mm.
Wratten filter: H-blue green.
Magnification: 170 diameters.

Fig. 72 shows a section of calf skin which had been soaked in sodium hydroxide solution previous to digestion with pancreatin at 40° C., under toluene. Not only is the epidermis destroyed and the hair loosened, but the skin is completely bated, as shown by the absence of elastin fibers.

An interesting attempt to unhair skins by means of enzymes naturally occurring in the skin is that of H. C. Ross.[23] A 1-per cent solution of ammonium hydroxide is used to inactivate the foreign enzymes, while the thrombase found in the skins is activated by the addition of calcium lactate or polysulfide. It is mentioned that the thrombase may be assisted by the addition of trypsin or other proteolytic enzymes which will work in an alkaline medium. The unhairing is effected without destroying the epidermis, so that large sections thereof can be removed with the hair attached. Subsequent bating is unnecessary. In preparing dressing leathers, the solutions are heated, while for sole leathers cold liquids are employed, these allowing plumping to take place to a greater extent. How nearly the actual mechanism of this method of unhairing is suggested by the description of the patent is open to question, but it would be interesting to see a study made of it along lines similar to those of the experiments of Wilson and Gallun.

Skins prepared for unhairing and scudding by means of pancreatin solutions are unhaired on a machine, scudded on the beam, and then washed, after which they are ready for tanning without further treatment. Skins from lime liquors are unhaired, scudded, washed and then either bated, delimed, drenched, or pickled before tanning. Some tanners put the skins directly into old vegetable tan liquors without giving them one of these treatments, but the tan liquor then becomes a deliming agent and has little value other than that of removing lime.

Apparently anything that will hydrolyze the newly formed cells of the epidermis without injuring the rest of the skin is a satisfactory unhairing agent. Lime owes its popularity to the safety attending its use. Its limited solubility makes it possible to maintain a constant hydroxide-ion concentration at about 0.03 mole per liter simply by using an excess. This concentration is high enough to retard putrefaction considerably and yet not great enough to injure the skin itself, since the solute is a diacid base. It is entirely possible, however, that the popularity of lime will wane when some of the newer methods of unhairing reach a higher stage of development.

[23] British Pat. 169,730, March 25, 1920. *Chemical Abstracts* 16 (1922), 853.

Chapter 9.

Bating.

Perhaps the most curious of all the processes involved in making leather is that of bating. Little is known of its origin because it was a secret process, but it is at least some centuries old. After the skins are taken from the lime liquors, unhaired, scudded, and washed, they still contain lime in the form of carbonate and in combination with the skin proteins. At this stage they are plump and rubbery and tanners have experienced many difficulties due to putting the stock directly into certain types of vegetable tan liquors when it was in this condition. The object of bating is to prepare the unhaired skins for tanning and originally consisted in keeping them in a warm infusion of the dung of dogs or fowls until all plumpness had disappeared and the skins had become so soft as to retain the impression of thumb and finger when pinched and sufficiently porous to permit the passage of air under pressure. When hen or pigeon manure was used, the process was called bating, and when dog dung was used, it was called puering, but the term bating is now applied to the process generally, regardless of the materials used. The difference in terminology naturally disappeared with the advent of artificial bating materials.

A common method for treating light skins was to put them into a vat filled with a liquor containing about 100 grams of dog dung per liter, kept at a temperature of 40° C. by means of steam. A paddle wheel kept the liquor and skins in motion. During the action, the skins gradually lost the plumpness acquired in the lime liquors and became soft and raggy. The completion of the process was determined by the attainment of a certain degree of flaccidity, which the workmen could judge only after long experience. Hen or pigeon manure was sometimes used for light skins, but was more commonly applied to heavy hides because it penetrates more rapidly than dog dung, due apparently to the fact that it contains also the urinary products, especially urea.

For many years this remained one of the mysterious processes of the tannery. It gave some tanners an improved product, which they could get in no other way known to them. But during the past thirty years there has been a persistent effort to determine the essential reactions of bating so that it might be carried out more reliably and with less offensive materials, or that it might be done away with

entirely by treating the skins differently at other stages. For example, it had been suggested that the only important function of the bate is the removal of the insoluble lime compounds from the skin before tanning. But this was contested by those who believed that merely removing the lime was not sufficient. They regarded bating as a process necessary for the removal of certain undesirable protein constituents of the skin. In order to settle this question, investigators have made extensive studies of dungs, and of the skins and liquors, both before and after the process.

The greatest pioneer work in this field has been carried out by J. T. Wood, whose investigations, coupled with practical developments by O. Röhm and others, have led to the almost complete replacement of the obnoxious dungs by pancreatic enzymes. In his book, Wood[1] says: "When learning the trade as an apprentice every fault in the leather was attributed to this part of the work, and the troubles and miseries of the 'puer shop' first caused me to take up the study of puering. I was determined to know the causes underlying the process. Puering is not only a filthy and disgusting operation, but is prejudicial to health, and in the nature of it is attended by more worry and trouble than all the rest of the processes in leather making put together."

Wood found the mineral matter of dungs to consist chiefly of the sulfates, chlorides, carbonates, and phosphates of sodium, potassium, ammonium, and calcium, and some silica. The most important organic constituents seemed to be the bacteria, enzymes, cellulose materials, and fats. He found both peptic and tryptic enzymes, a rennin, an amylolytic enzyme, and a lipase. Since the bate liquor is usually faintly alkaline, it seemed likely that trypsin was active in the process and it was later shown that this enzyme does produce some of the effects of dung upon the skin. Wood also isolated from dog dung a species of *B. coli* which was found to yield an enzyme capable of acting upon the skin like trypsin.

Artificial bates are now to be found upon the market which contain pancreatin, ammonium chloride, and supposedly inert fillers and these have largely supplanted the dung bates formerly used. But materials other than those containing tryptic enzymes have also appeared on the market, as bates, to revive the old question as to the fundamental object to be attained by bating. These materials apparently give satisfactory results for some kinds of leather, even though some of them consist merely of carbohydrates, which yield organic acids by fermentation. The dung bates evidently had several different functions, but apparently all manufacturers of artificial bating materials did not concentrate their attentions upon the same functions. Numbers of preparations of quite different properties are sold as bating materials and this has served to aggravate the confusion as to what constitutes a bating material. The several purposes served by these materials will be considered separately.

[1] The Puering, Bating and Drenching of Skins. J. T. Wood. E. & F. N. Spon, London (1912).

Falling.

The one property which all of the various types of bating materials have in common is that of reducing the degree of swelling of the protein constituents of the limed skin, which action is known to the trade as *falling*. Indeed it would have been practically impossible for any artificial preparation to pass as a bate that did not have this property, because the degree of flaccidity of the skin was the accepted measure of the nearness to completion of the bating process.

It will be apparent from the discussion of the swelling of protein jellies given in Chapter 5 that the degree of falling of a skin must be a function of hydrogen-ion concentration and also of the concentration of neutral salts.

Wilson and Gallun [2] measured the degree of plumping of calf skin as a function of pH value by means of their method, which is described in Chapter 8. Pieces of unhaired skin, each about 2 centimeters square, were cut from the butt of a calf skin so as to insure the greatest degree of uniformity of structure. These were freed from lime by washing in a 12-per cent solution of sodium chloride containing a small amount of hydrochloric acid, and then neutralized in cold, saturated sodium bicarbonate solution. They were then washed and bated by keeping at 40° C. for 24 hours in a solution containing 0.1 gram of U.S.P. pancreatin, 2.8 grams of monosodium phosphate, and 18 cubic centimeters of molar sodium hydroxide solution per liter, giving a pH value of 7.7. Microscopic examination showed that this procedure removed all of the elastin fibers. The pieces were then washed in cold, running tap water, having a pH value of 8, for 24 hours. They were then kept in distilled water in the refrigerator at 7° C. until used for the tests. The condition in which the skin existed in this state was taken as a standard, as it was found to be easily reproducible.

A series of 24 large reservoirs of test solutions was prepared, each having a final concentration of tenth-molar phosphoric acid plus the amount of sodium hydroxide required to give the desired pH value as determined by the hydrogen electrode. A range of pH values from 4 to 11 was covered.

In each test a piece of skin in standard condition was placed in the Randall and Stickney thickness gauge described in Chapter 8. The gauge reading in every case was taken exactly five minutes after dropping the plunger onto the piece of skin. This was called the initial gauge reading. The skin was then shaken with water to bring it back to its natural shape and then put into 200 cubic centimeters of standard buffer solution of the desired pH value and kept in a thermostat refrigerator at 7° C. so as to reduce to a minimum any tendency towards putrefaction. After 24 hours, each solution was replaced by fresh buffer solution. After 4 days more, there being

[2] The Points of Minimum Plumping of Calf Skin. J. A. Wilson and A. F. Gallun, Jr. *Ind. Eng. Chem.* 15 (1923), 71.

practically no change taking place in the pH values of the solutions, it was assumed that equilibrium was established and the pieces were removed and their thicknesses measured again. The results are given in Table XVI. The ratio of the final to the initial gauge reading is a measure of the degree of plumping of the skin and this is plotted as a function of the pH value in Fig. 73.

TABLE XVI.

Unhaired Calf Skin in Contact with Buffer Solutions of Different pH Values.

Gauge readings in mm. (average of duplicates)			pH value of solution at 20° C.	
Initial	Final	Ratio *	Initial	Final
1.421	2.729	1.92	3.96	3.97
1.205	1.885	1.56	4.14	4.17
1.269	1.431	1.13	4.47	4.49
1.439	1.296	0.90	4.78	4.79
1.489	1.305	0.88	5.08	5.07
1.299	1.161	0.89	5.29	5.27
1.347	1.239	0.92	5.57	5.57
1.388	1.306	0.94	5.78	5.72
1.212	1.263	1.04	6.04	6.08
1.225	1.270	1.04	6.29	6.29
1.391	1.478	1.06	6.48	6.42
1.248	1.343	1.08	6.69	6.68
1.435	1.514	1.06	6.96	6.88
1.292	1.362	1.05	7.08	7.00
1.379	1.415	1.03	7.41	7.41
1.413	1.385	0.98	7.68	7.62
1.393	1.407	1.01	7.97	7.89
1.515	1.520	1.00	8.42	8.44
1.428	1.427	1.00	8.56	8.50
1.253	1.343	1.07	9.03	9.13
1.258	1.377	1.09	9.59	9.64
1.219	1.388	1.14	10.00	9.98
1.240	1.621	1.31	10.47	10.51
1.280	2.206	1.71	11.06	11.08

* This ratio is a measure of the degree of plumping of the skin.

The significance of these two points of minimum plumping has been discussed in Chapter 5. By comparing Fig. 73 with Fig. 45, it will be seen that the plumping of calf skin varies in much the same way as the swelling of gelatin with change of pH value. Apparently collagen undergoes a change of form, possibly an internal rearrangement, in passing from an acid to an alkaline solution and the two points of minimum represent the isoelectric points of the two forms.

The degree of plumping at any point between 4.5 and 9.0 is relatively so small that the skin would pass as completely bated, if judged solely by its *fallen* condition. Wood, who was probably the first to apply the hydrogen electrode to tannery liquors, observed that the pH value of fresh dung bate liquors varied from about 4.7 to 5.4, whereas the bating of a pack of skins raised it to points lying

between 6.4 and 8.4. In a lime liquor, which has a pH value of about 12.5, the skin is very plump and rubbery. But when it is brought into equilibrium with a liquor having a pH value lying between 4.5 and 9.0, it becomes fallen and flaccid.

The author has observed that when putrefaction starts in protein solutions the pH value of the solution generally tends to shift into the region 5.5 to 6.0, regardless of what it may have been in-

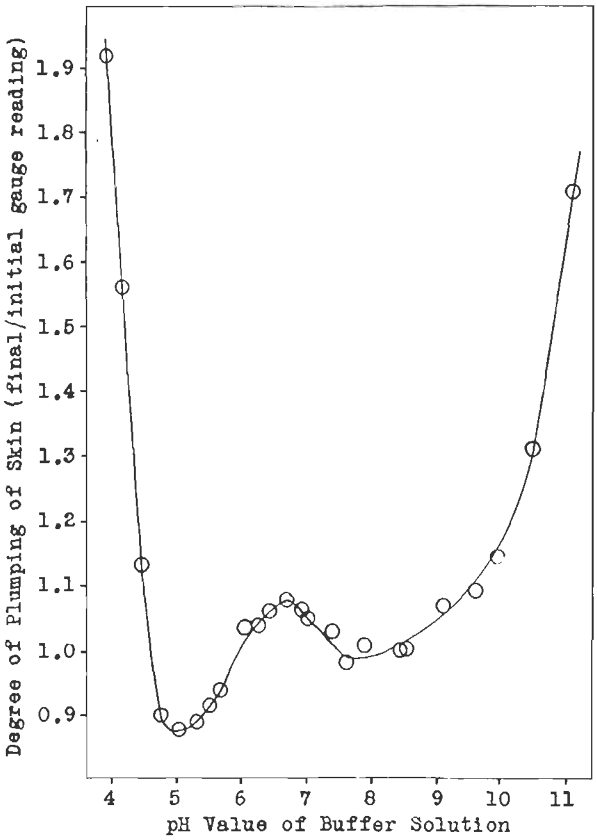


FIG. 73.—Showing the two points of minimum plumping of calf skin.

itially. The putrid dung bates would, therefore, tend to reduce the pH value of the limed skin from 12.5 to a value approaching 6. But the bate liquor contains phosphates, which act as buffers, and the full drop in pH value is prevented. The phosphate is thus a safeguard against putrefaction of the skin, which would be quickly damaged if the pH value were allowed to drop to the range of maximum rate of putrefaction.

Many so-called bating materials probably serve chiefly to reduce the pH value of limed skins to the region of minimum plumping. The value of this fallen condition is readily apparent for skins which are to be tanned in vegetable tan liquors. Tannins diffuse only very slowly through swollen skin, but when the skin is in a fallen condition, the tannins are enabled to diffuse rapidly into the spaces between the fibers, greatly hastening complete penetration. There is a fallacy in the assumption that plump leather can be produced only by putting skin into the tan liquors in a plump condition. The solidity of the resulting leather is determined more by the reaction of the liquor itself than by the degree of plumping of the skin when first put into the liquor.

The manufacture of materials capable of bringing limed skin int the condition of minimum plumping is obviously a simple matter. I is only necessary to incorporate a buffer material with one whic will tend to lower the pH value of the limed skin to a final value o about 8. Among the materials used for this purpose are boric acic ammonium chloride, weak organic acids and materials yielding acid by fermentation, and acid sodium phosphate. The author observe five successive lots of skins pass through an artificial bate liquor con taining sodium phosphate, which was entirely uncontrolled, and 0. was the greatest deviation in pH value from the normal value of 8. during the entire period of operation. Where it is desired only t bring the skins into a fallen condition, the process can be carrie out very effectively using only sodium phosphate and the occasiona addition of hydrochloric acid to maintain a pH value of about 8.

Regulation of Hydrogen-Ion Concentration.

Although the degree of plumping of a skin is a function of th hydrogen-ion concentration, the action of a bate liquor in lowerin the pH value of limed skin has an importance independent of th question of plumping. Nearly 80 per cent of the bated weight of skin is due to water, or rather bate liquor. Even though the ski may be washed, the water will assume a pH value depending upo the substances held in combination with the skin. This adherin solution will therefore have an effect upon the tan liquor into whicl the skins are put. If the pH value of this adhering solution is ver variable, difficulty will be experienced in vegetable tanning becaus the rate of tanning, the rate of diffusion of the tan liquor into th skin, the color value of the tan liquor, and its tendency to oxidiz are all functions of the pH value. Keeping constant the pH valu of the solution adhering to the skins entering the tan liquors is factor of great importance and one which made the old dung bate almost a necessity to the tanner who had no other way of controllin the pH value. The actual pH value, within limits, was probably o less importance than keeping it constant at some arbitrary value, whicl could be met by establishing conditions in the tan yard to correspond

Deliming.

Many persons have looked upon bating chiefly as a process for removing the combined lime from the skins. In using a dung bate, Wood found from 3 to 6 per cent of lime, calculated as calcium oxide on the dry skin, before bating and only from 0.5 to 0.9 per cent after bating and all of this appeared to be present as neutral salt.

Artificial bates, however, do not all have the property of removing calcium from the skin. Upon investigating the operation of a bate liquor containing phosphates and ammonium chloride and having a pH value of 8.4, the author found no diminution of the calcium content of the skin during bating, although the skins had become completely fallen and practically all of the lime had been converted into neutral or insoluble salts. Apparently insoluble calcium phosphate had formed in the skin, where it remained. In cases like this, the process can hardly be called efficient as a means of deliming. Where nearly complete removal of calcium compounds is essential for the best operation of later processes, it is much better to employ a properly controlled acid liquor, such as those to be described in the next chapter.

Bacterial Action.

Bacteria play an important rôle in the action of dung bates, being instrumental in the removal of lime from the skin as well as in lowering the pH value to the region of minimum plumping. Some of the bacteria, or their products, also attack portions of the skin itself, as shown by the appearance of nitrogenous matter in solution. In Fig. 74 is shown a typical plate culture on gelatin [3] of a dung bate liquor in actual use.

Becker [4] isolated 54 varieties of bacteria from dog dung and studied the actions of many of them upon skin. He found one, which he called *B. erodiens*, capable of producing a falling action of limed skin similar to that of the dung bate itself. An artificial bacterial bate was developed independently by Wood in England and by G. Popp and H. Becker in Germany, but they later joined forces and perfected the artificial bate known as erodin, which consists of a nutrient material to which a pure culture of *B. erodiens* is added before using. This material has been used on a commercial scale and found to be a satisfactory substitute for dung for some kinds of leather.

Since *B. erodiens* does not secrete tryptic enzymes, Wood has suggested adding to it bacteria obtained from the roots of wool in the sweating process which secrete a mild form of proteolytic ferment. The susceptibility of erodin liquors to become contaminated by foreign bacteria presents an obstacle to any very widespread increase in their use. In using erodin, Wood has observed that the fresh liquor

[3] Cf. The Properties and Action of Enzymes in Relation to Leather Manufacture. J. T. Wood. *J. Ind. Eng. Chem.* 13 (1921), 1135.

[4] Bacteriological Reactions in the Leather Industry. H. Becker. *Z. öffent. Chem.* 10 (1904), 447.

usually has a pH value of about 6.6 and this increases to about 7.3 during the bating operation.

Cruess and Wilson[5] isolated 10 varieties of bacteria from pigeon dung and found that the falling of limed skins could be brought about by pure cultures in dilute skim milk. If the bating operation were unduly prolonged, the skin proteins became hydrolyzed, but they found

Fig. 74.—Typical Plate Culture on Gelatin of Puer Liquor.

that danger from this source could be greatly minimized by using a liquor containing 0.5 per cent of glucose. They pointed out that the glucose was decomposed into acids which checked bacterial action and assisted in the removal of lime from the skin.

The prevailing opinion is that bating is not produced directly by the bacteria, but rather by the products which they secrete. Of these, the enzymes are regarded as the most important because the reduction in pH value of the skin, with consequent falling, can be brought about by simple chemical means not generally regarded as constituting the process of bating.

[5] A Bacterial Study of the Bating Process. W. Cruess and F. H. Wilson. *J. Am. Leather Chem. Assoc.* 8 (1913), 180.

Enzyme Action and Elastin Removal.

Wood [6] separated the enzymes from dog dung by precipitation from solution with alcohol and showed that the enzymes, in conjunction with ammonium compounds, were capable of bating skins. In view of the fact that the bate liquor was alkaline, it seemed pretty certain that trypsin must be the principal enzyme acting. Wood and Law [7] later showed that there were at least five different enzymes present in dog dung, as follows:

1. A peptic enzyme resembling stomach pepsin.
2. A tryptic enzyme resembling pancreatic trypsin.
3. A rennin (coagulating enzyme).
4. An amylolytic enzyme.
5. A lipase.

Where a skin contains an abundance of fat cells, the lipase probably exerts an important function in hydrolyzing and emulsifying the fats.

In 1908 Röhm [8] patented the use of the enzymes of the pancreatic juice and ammonium salts as a bating material. This mixture now known as oropon has come into wide use and has largely supplanted the dung bates formerly used.

Recently there has been a concerted effort to determine just what part is played by pancreatin in the bating process. As a measure of the elastin content of skin, Rosenthal [9] used the per cent of nitrogenous matter that could be rendered soluble by tryptic digestion. By this method he found that bating with oropon reduced the elastin content of calf skin from 10.36 to 0.31 per cent, calculated on the dry basis. The author's later investigations of the bating process by means of the microscope, however, indicate that Rosenthal's method of determining the elastin content of skin is unreliable. Apparently a large portion of the matter included as elastin was derived from the other protein constituents of the skin or their hydrolytic products.

Upon examining a dung bate liquor used to bate sheep grains, Wood found that nitrogenous matter had been dissolved equivalent to only one per cent of the total protein matter of the skins. As nearly as can be judged from microscopic observations, this represents approximately the percentage of elastin present in the skin.

Seymour-Jones [10] also suggested that the function of bating is the removal of the elastin fibers of the skin. In collaboration with J. T. Wood, Seymour-Jones carried out an interesting experiment on the bating of sheep skin. The "flywing" grain of a sheep skin was split from the main body of the skin, called simply flesh for convenience,

[6] Notes on the Constitution and Mode of Action of the Dung Bate. J. T. Wood. *J. Soc. Chem. Ind.* 17 (1898), 1011.

[7] Enzymes Concerned in the Puering or Bating Process. J. T. Wood and D. J. Law. *J. Soc. Chem. Ind.* 31 (1912), 1105.

[8] U. S. Pat. 886,411, May 5, 1908.

[9] Biochemical Studies of Skin. G. J. Rosenthal. *J. Am. Leather Chem. Assoc.* 11 (1916), 463.

[10] The Physiology of the Skin. Alfred Seymour-Jones. *J. Soc. Leather Trades Chem.* 4 (1920), 60.

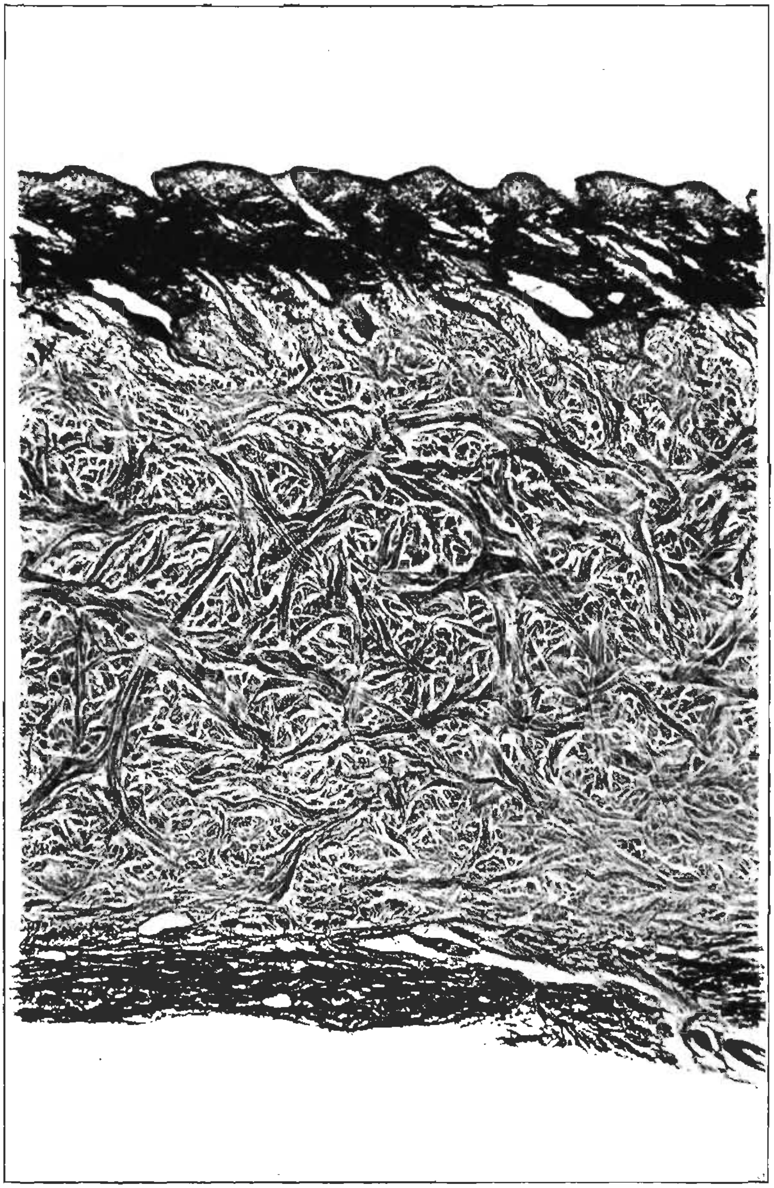


Fig. 75.—Vertical Section of Calf Skin.
(After liming and unhairing, before bating.)

Location: butt.
Thickness of section: 40 μ.
Stains: Weigert's resorcin-fuchsin and picro-red.
Eyepiece: none.
Objective: 32-mm.
Wratten filters: B-green; E-orange.
Magnification: 25 diameters.

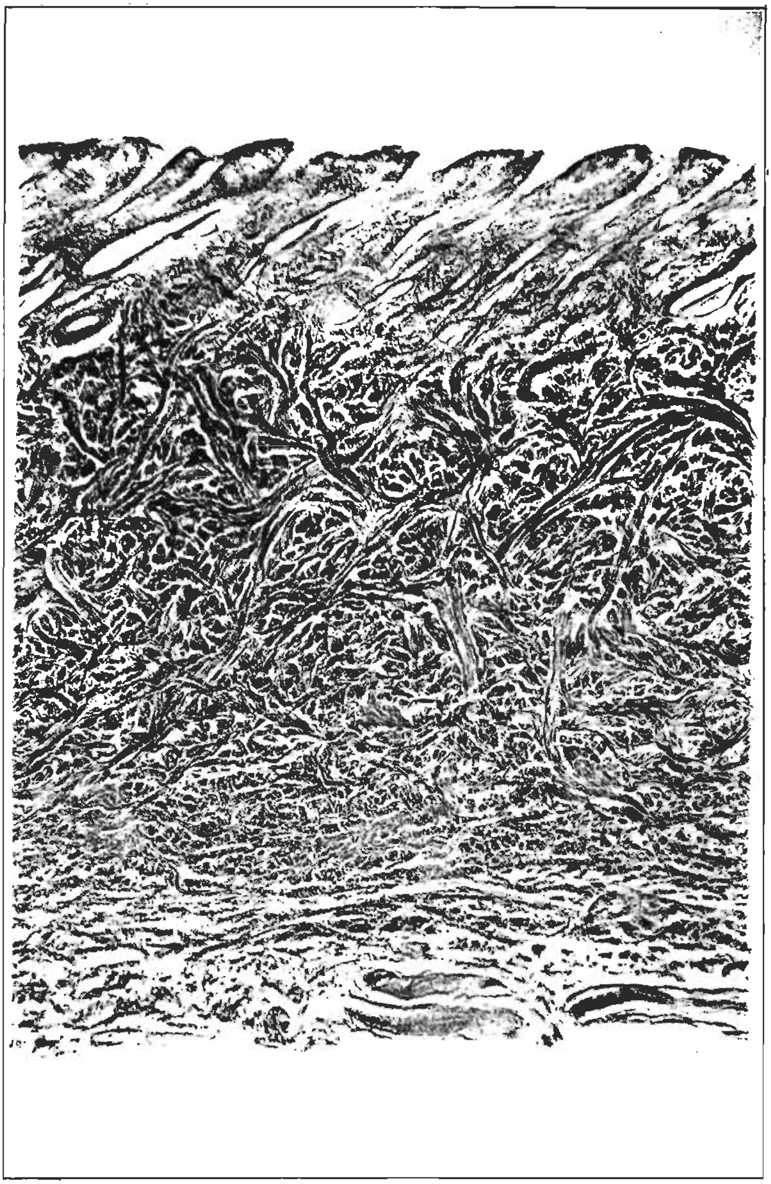


Fig. 76.—Vertical Section of Calf Skin.
(After bating, before tanning.)

Location: butt.
Thickness of section: 40 μ.
Stains: Weigert's resorcin-fuchsin and picro-red.
Eyepiece: none.
Objective: 32-mm.
Wratten filters: B-green; E-orange.
Magnification: 25 diameters.

and both grain and flesh were cut into halves along the backbone. One grain and one flesh were bated with pancreol, a pancreatin preparation similar to oropon, while the other halves were delimed with acetic acid, but not bated. All four pieces were then tanned with sumac. There was comparatively little difference between the bated and unbated flesh halves, but the grain samples were very different from each other. The bated grain was soft and even, with the hair-holes clean and clear, but in the unbated grain the hair-holes appeared to be glued up and the surface had a rough, contracted appearance. He concluded that elastin present in the region of the grain membrane must be digested before tanning in order to produce a satisfactory grain surface, but that the bating of the skin under the grain is not only unnecessary, but often undesirable.

The difference which Seymour-Jones found between the two grains was probably not due entirely to the bating process, since one was treated with acetic acid while the other was not. This means that the unbated grain would be subjected to the action of tan liquor at a lower pH value than the bated grain. But as the pH value of a fresh tan liquor is lowered, there is an increasing tendency for it to produce in the grain layer of a skin the rhythmic swelling described in Chapter 5. This shows itself first in a roughening of the grain, similar to that described by Seymour-Jones, and with further drop in pH value the corrugation of the surface appears. The roughening of the grain which had not been bated may have been aggravated by the presence of the elastin fibers, but the chief cause was probably the lower pH value.

Wilson and Daub [11, 12] undertook to settle definitely the question of the removal of elastin in the bating process by means of the microscope. They prepared sections of calf skin taken both before and after bating with a solution of pancreatin and found that the process removes all of the elastin fibers, if sufficiently prolonged. Fig. 75 shows a section of calf skin taken after liming, unhairing, scudding, and washing, but before bating. The elastin fibers show as a thick, black band just under the grain surface; the magnification here is not sufficiently great to show each individual fiber. Another layer of elastin fibers appears at the flesh boundary. The main body of the skin contains no elastin fibers excepting those surrounding blood vessels, nerves, and muscles. Fig. 76 shows an adjoining section of the same skin taken after bating for 24 hours in 0.01-per cent pancreatin solution at 40° C., having a pH value of 7.5.

The author has recently received a letter from Mr. L. Krall of Geneva, Switzerland, claiming priority in discovering, by means of the microscope, that the chief function of bating is the removal of elastin fibers from the skin. His experiments, performed at the University of Geneva from 1914 to 1916, proved that the elastin fibers of skin can be entirely removed by digestion in an infusion of dog dung at 40° C. His photomicrographs show that the action of dung is

[11] The Mechanism of Bating. J. A. Wilson. *J. Ind. Eng. Chem.* 12 (1920), 1087.
[12] A Critical Study of Bating. J. A. Wilson and Guido Daub. *Ibid.*, 13 (1921), 1137.

practically identical with that found by Wilson and Daub for pancreatin, thus furnishing further evidence of the soundness of Wood's conclusion that pancreatin is the active constituent of dung in bating. Krall's important paper [13] was unfortunately buried in a private bulletin.

After examining hundreds of sections of skin, taken before and after bating, at high magnifications and with the employment of a great variety of stains, Wilson and Daub came to the conclusion that the removal of elastin is the primary function of bating and that the other actions associated with dung bates can all be produced by the simple chemical control of the processes other than bating. The falling of the skin, however, always accompanies the removal of elastin because the range of pH values over which pancreatin acts upon elastin is such as to reduce the plumping of limed skin to the point accepted as a measure of the completion of the bating process.

In studying the progress of bating, Wilson and Daub observed cross sections of skin taken before and after bating and estimated the per cent of elastin removed by the treatment. For this purpose, the sections were prepared and stained as described in Chapter 2. The enzyme which they employed was a commercial sample of U.S.P. pancreatin which showed by analysis: water, 6.3 per cent; ash, 6.8 per cent; nitrogen, 11.0 per cent; chlorine, 1.7 per cent; phosphates, as phosphorous pentoxide, 3.5 per cent; sulfate, none. By the method for determining tryptic activity described by Sherman and Neun,[14] 10 milligrams of the sample acting upon 1 gram of casein in 100 cubic centimeters of solution for 1 hour at 40° C. and at pH value of 7.33 digested 51 milligrams of nitrogen. As a matter of caution, it should be pointed out that this does not give a correct measure of the activity of the enzyme so far as its power to digest elastin is concerned. The author suggests that the elastin-digesting power of a bating material be determined solely by the amount of elastin which a given sample can digest from skin under rigidly defined conditions. The activity of the sample on casein or gelatin may be entirely misleading as regards its value as a bating material.

For each series of experiments, Wilson and Daub cut a piece of limed and unhaired calf skin into strips about 2 x 0.5 inches. There is a small, but appreciable, difference in time required for complete removal of elastin from skins of different thickness and for this reason care was exercised in selecting all strips for any one series from the same part of the same skin, so as to have them all as nearly identical as possible. Each strip was put into 500 cubic centimeters of liquor, a volume large enough to prevent the skin from seriously altering the concentration of the liquor. The liquors were all put into dark brown bottles to shield them from the light and were kept in a large Freas thermostat for the stated lengths of time at $40° \pm 0.01°$ C., the optimum temperature for most enzyme actions.[15]

[13] Ferments in the Tannery. L. Krall. *Societe Anonyme, anc. B. Siegfried.* Zofingue, Switzerland. Private bulletin, June, 1918.
[14] H. C. Sherman and D. E. Neun. *J. Am. Chem. Soc.* 38 (1916), 2199.
[15] The Chemistry of Enzyme Actions. K. G. Falk. The Chemical Catalog Co., New York.

Every liquor contained 0.02 mole per liter of added phosphoric acid to act as a buffer, in addition to the enzyme, and the potassium hydroxide required to give the desired hydrogen-ion concentration. The pH value of each liquor was determined both before and after the digestion period by means of Hildebrand electrodes and a Leeds and Northrup potentiometer, excepting where it was proved by previous test that the results obtained by the Clark and Lubs series of indicators were sufficiently accurate. Except for the more strongly acid and alkaline solutions, the change in pH value during digestion was practically negligible. Estimates of the per cent of elastin removed were made on the basis of removal from the grain layer only. In some cases all of the elastin was removed from the grain layer before half of it was removed from the flesh layer. Since the shaving operation removes practically all of the flesh elastin, its removal in bating is of little importance.

As a rule, a preliminary series covering a very wide range was run, followed by a second series covering only the active range of the enzyme. A third series was usually run as a check.

Effect of Hydrogen-Ion Concentration.

It is well known that the hydrogen-ion concentration is an important factor in determining the rate of digestion by enzymes. Using 0.1 gram of pancreatin per liter and digesting for 24 hours, complete removal of elastin from the skin was obtained only between the pH values 7.5 and 8.5. A portion of the pancreatin was put into a collodion sac and dialyzed against running tap water in a dark room for 16 hours and used in a duplicate series in such quantity as to represent 0.1 gram per liter of the original pancreatin. The results were identical with those obtained with the undialyzed enzyme. A series was then run in which the concentration of pancreatin was increased to 1.0 gram per liter. Complete removal of elastin was obtained between the pH values 5.5 and 8.5. The results of the two series, which are shown in Fig. 77, were carefully checked to insure their accuracy. The per cent of the total elastin which was removed is plotted against the pH value of the solution taken after digestion and cooling to 25° C.

The peculiar relation of the curves to each other is significant. They nearly coincide at all pH values above 7.5, but at 6.0 the stronger solution is still at its optimum activity, while the weaker one has apparently entirely lost its elastin-digesting power. When an enzyme has been found to have different optimum pH values with different substrates, it has been supposed that the effect of the hydrogen-ion concentration upon the substrate has been the determining factor. But here we have the same enzyme and the same substrate, with a change in the optimum range due merely to a change in concentration of the enzyme.

An explanation is suggested by the work of Northrop,[16,17] who has shown that the activity of an enzyme solution is not necessarily a function of the apparent total enzyme concentration, but that a portion of the enzyme may be inactivated by combining with peptone or other foreign matter. He has pointed out further that the extent of the formation of addition compounds between protein and enzyme depends upon the concentration of protein ion, which in turn is a function

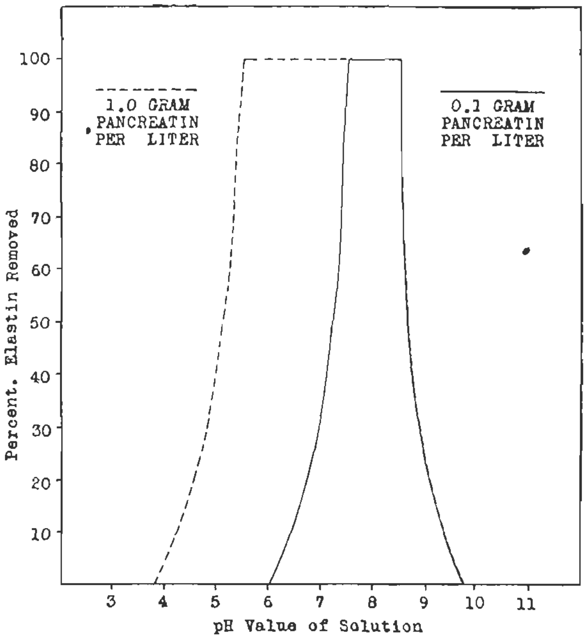


FIG. 77.—Removal of elastin fibers from limed calf skin as a function of hydrogen-ion concentration. Time of digestion 24 hours; Temperature 40° C.

of the hydrogen-ion concentration. If some protein other than elastin is responsible for the inactivation of a portion of the enzyme, we should expect such action to be a minimum at the isoelectric point of this protein.

After bating, the strips of calf skin were all carefully examined for the "bated feel," which apparently bears no relation to elastin removal, but corresponds to a condition of minimum swelling of the skin proteins. The only strips passing this test were those from liquors having pH values between 6.1 and 9.8. The average of these is 8, which is also the midpoint of the optimum range for the more dilute enzyme solution. This value evidently corresponds to the sec-

[16] The Effect of the Concentration of Enzyme on the Rate of Digestion of Proteins by Pepsin. J. H. Northrop. *J. General Physiol.* 2 (1920), 471.
[17] The Significance of the Hydrogen-Ion Concentration for the Digestion of Proteins by Pepsin. *Ibid.*, 3 (1920), 211.

ond point of minimum plumping of calf skin found by Wilson and Gallun and shown in Fig. 73. It is worthy of note that at 40° C. Wilson and Daub found no indication of a point of minimum except at 8. On the basis of the theory of the existence of two forms of collagen, discussed in Chapter 5, it would appear that at 40° Wilson and Daub were dealing only with the form stable at higher temperatures and pH values and whose isoelectric point appears to be at 7.7.

The following explanation is therefore suggested tentatively. At a pH value of 7.7, practically all of the enzyme is left free to attack

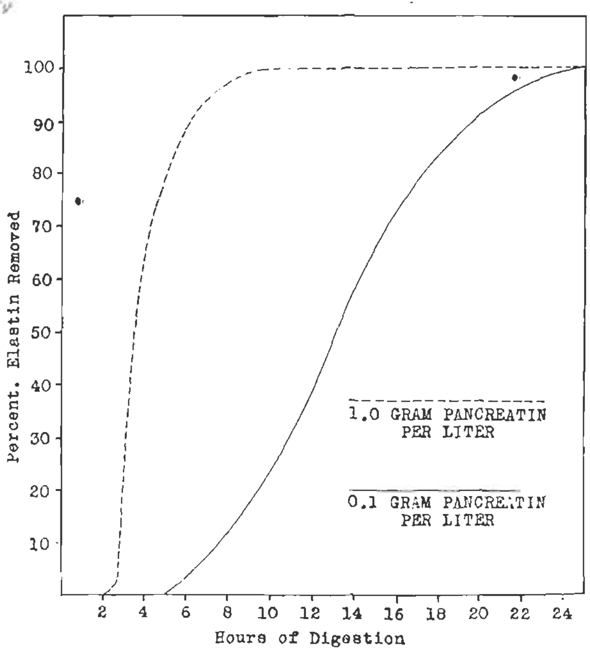


FIG. 78.—Removal of elastin fibers from limed calf skin as a function of time of digestion. Temperature 40° C.; pH value 7.6.

the elastin, but as the pH value is decreased and the concentration of collagen cation correspondingly increased, more and more enzyme is removed from the field of action by combining with it. In the weaker enzyme solution at pH = 6 practically all of the enzyme is in combination with collagen, whereas in the stronger solution the excess of enzyme is still sufficient to digest elastin. It is interesting also to note that Thomas and Seymour-Jones [18] found that pancreatin attacks collagen at an increasing rate as the pH value is lowered from 8 to 6. In dealing with the effect of hydrogen-ion concentration upon enzyme action, it is evidently necessary to know the effect of the

[18] Hydrolysis of Collagen by Trypsin. A. W. Thomas and F. L. Seymour-Jones. *J. Am. Chem. Soc.* (1923); (advance copy).

hydrogen-ion concentration upon each substance in contact with the solution.

It is interesting to compare the optimum pH values for tryptic digestion found by other investigators:[19] for albumose Michaelis and Davidsohn[20] found 7.7; for casein Sherman and Neun[21] found 8.3, while Long and Hull[22] found 5.5 to 6.3; and for fibrin Long and Hull[22] found 7.5 to 8.3. The total range of 5.5 to 8.3 corresponds closely to the range found by Wilson and Daub, 5.5 to 8.5, for complete removal of elastin by the more concentrated enzyme solution.

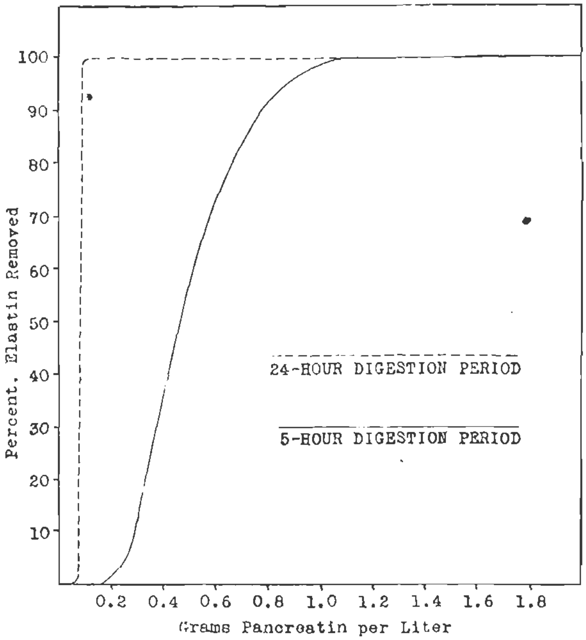


FIG. 79.—Removal of elastin fibers from limed calf skin as a function of concentration of enzyme. Temperature 40° C.; pH value 7.6.

At pH values less than 3.0 there was a marked destruction of the collagen fibers, evidently due to acid hydrolysis, and the strips were much swollen and rubbery, but no removal of elastin could be detected.

Effect of Time of Digestion.

Two series of solutions were prepared, one in which the concentration of enzyme was 0.1 gram per liter and the other in which it was 1.0. All members of both series were otherwise identical. The

[19] Cf. Falk, *loc. cit.*, p. 66.
[20] *Biochem. Z.* 36 (1911), 280.
[21] *J. Am. Chem. Soc.* 38 (1916), 2203; 40 (1918), 1138.
[22] *Ibid.*, 39 (1917), 1051.

pH value of each liquor was brought to 7.6 and this did not change during digestion. Each strip of calf skin was kept in a separate bottle. The bottles were removed from the thermostat at fixed intervals during 24 hours.

Complete removal of the elastin was effected by the stronger enzyme solution in 6 to 8 hours, but in the weaker solution 24 hours were required. The progress of the digestion is shown in Fig. 78. The time required to start the digestion, 2 hours for the stronger and 5 hours for the weaker solution, was apparently the time required for

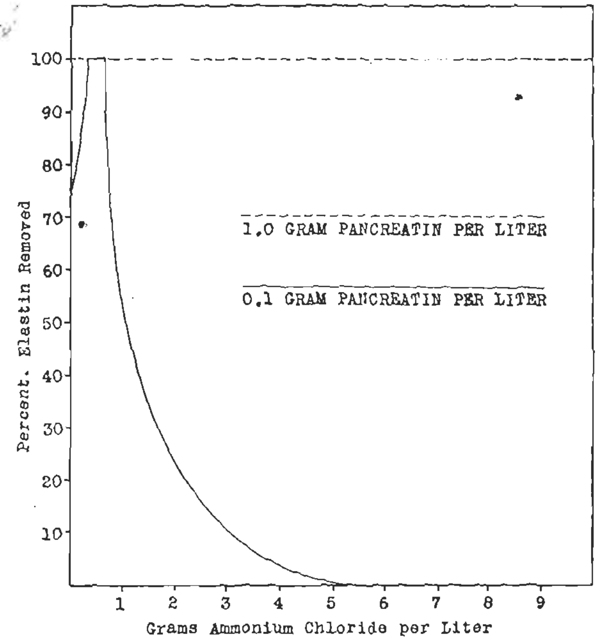


FIG. 80.—Removal of elastin fibers from limed calf skin as a function of the concentration of ammonium chloride. Time of digestion 24 hours; Temperature 40° C.; pH value 7.6.

the enzyme to diffuse into the region of the skin containing the elastin fibers. As will be seen from Fig. 82, these begin about 0.1 millimeter below the grain surface.

Effect of Concentration of Enzyme.

Two identical series of solutions were prepared in which the individual members differed only in concentration of pancreatin. One series was kept in the thermostat for 5 hours and the other for 24 hours. The results are shown in Fig. 79 and furnish a study in economy. Complete removal of elastin is effected by 0.1 gram of pancreatin in 24 hours or by 1.1 grams in 5 hours.

Effect of Concentration of Ammonium Chloride.

A study of bating would not be complete if it did not include the effect of ammonium chloride, one of the most abundant constituents of commercial bating materials. Aside from its use as a filler, it has been assumed to be beneficial in removing lime from the skins and tending to maintain a slight alkalinity favorable to tryptic digestion. Two series of solutions were prepared in which the concentration of enzyme was 0.1 and 1.0 gram per liter, respectively. To each successive member of each series increasing amounts of ammonium chloride were added and the pH values of all members were brought to 7.6. The time of digestion was 24 hours. The results are shown in Fig. 80.

In working with very dilute enzyme solutions, a distinct activating effect was noted upon the addition of 0.5 gram per liter of ammonium chloride, while larger amounts showed an inhibitory effect. With thin calf skin the activating effect was not detectable with the solution containing 0.1 gram per liter of enzyme after a 24-hour digestion period, because all of the elastin was removed without adding any ammonium chloride. In order to show the activating effect in these experiments, strips from heavier skins were used, which require a somewhat longer time for complete removal of elastin under fixed conditions. The activating effect of 0.5 gram of ammonium chloride per liter and the inhibitory effect of greater concentrations are very marked. It is also important to note that the effect of ammonium chloride can be entirely overcome by a sufficient excess of enzyme.

This behavior of ammonium chloride is interesting in view of the finding of Thomas[23] that potassium bromide in concentrations of 0.0 to 0.1 mole per liter has an inhibitory effect upon the action of malt amylase, but in greater concentration has an activating effect.

At concentrations greater than 50 grams per liter the ammonium chloride exerted a destructive action upon the collagen fibers, probably due to the formation of free ammonia.

Distribution of Elastin Fibers in the Skins of Different Animals.

It is well appreciated by tanners that skins of different animals and of animals of different ages must be treated differently in bating, as well as in other processes. It has been noted, for example, that the bating of a cow hide is less effective than the bating of a calf skin under the same conditions. The reason for this will be made apparent by comparing Figs. 81 and 82, both of which were photographed at exactly the same magnification. They represent the upper portions of the skins taken after liming, unhairing, scudding, and washing, but before bating. Fig. 81 is from a full grown cow hide,

[23] A Noteworthy Effect of Bromides upon the Action of Malt Amylase. A. W. Thomas. *J. Am. Chem. Soc.* 39 (1917), 1501.

Fig. 81.—Vertical Section of Thermostat Layer of Cow Hide.
(After liming and unhairing, before bating.)

Location: butt.
Thickness of section: 20 μ.
Stain: Daub's bismarck brown.

Eyepiece: 5X.
Objective: 16-mm.
Wratten filter: C-blue.
Magnification: 140 diameters.

Fig. 82.—Vertical Section of Thermostat Layer of Calf Skin.
(After liming and unhairing, before bating.)

Location: butt.
Thickness of section: 20 μ.
Stain: Daub's bismarck brown.

Eyepiece: 5X.
Objective: 16-mm.
Wratten filter: C-blue.
Magnification: 140 diameters.

Fig. 83.—Vertical Section of Thermostat Layer of Sheep Skin.
(After liming and unhairing, before bating.)

Location: butt.
Thickness of section: 20 μ.
Stain: Daub's bismarck brown.

Eyepiece: 5X.
Objective: 16-mm.
Wratten filter: C-blue.
Magnification: 140 diameters.

Fig. 84.—Vertical Section of Thermostat Layer of Hog Skin.
(After liming and unhairing, before bating.)

Location: butt.
Thickness of section: 20 μ.
Stain: Daub's bismarck brown.

Eyepiece: 5X.
Objective: 16-mm.
Wratten filter: C-blue.
Magnification: 140 diameters.

while Fig. 82 is from a young heifer calf skin. It will be noted that the older skin has relatively fewer elastin fibers, although they extend into the skin to a greater absolute depth. This greater depth necessitates leaving the hide in the bate liquor for a longer time, so that the enzyme may diffuse to the most deeply seated fibers, but, on the other hand, there is less reason for removing the elastin fibers from the heavier skin, because they are relatively fewer.

Fig. 83 shows the elastin fibers of a sheep skin before bating and Fig. 84 those of a hog skin. The elastin fibers of the hog skin are very sparsely scattered; the heavy band of elastin fibers passing obliquely upward to the right, across the center, is apparently there for the purpose of protecting the erector pili muscle, which it surrounds.

Figs. 81, 82, 83, and 84 should be compared with Figs. 11, 18, 28, and 30, respectively, of Chapter 2, which show sections taken from the same skins when fresh.

Effect of Elastin Removal on the Final Leather.

Wilson and Daub attempted to determine the practical value of bating by comparing bated and unbated skins. A limed calf skin was cut into halves along the line of the backbone, the elastin was completely removed from one half by means of pancreatin, while the other half, was simply treated with dilute ammonium chloride solution having a pH value of 8, in order to reduce its degree of plumping to that corresponding to what is accepted as the bated state. Both halves were then thoroughly washed. It was recognized that an exact comparison of the two halves during tanning could not be made, if the pH values of the absorbed solutions were very different. Every effort was made to have the pieces identical, excepting for elastin content.

The most noticeable difference was observed during the early stage of vegetable tanning. The surface layers of the skin naturally tan more rapidly than the fibers in the interior and there is a tendency for the grain surface to expand temporarily to a greater extent than the rest of the skin. The elastin fibers in the unbated half evidently tended to prevent this expansion and the result of the tension produced was a slightly harsh feel, although the grain appeared tight and smooth to the eye. The grain of the completely bated half, however, actually expanded, giving the skin temporarily a wrinkled appearance, although the grain felt very soft and silky. When both halves had become completely tanned, this difference had almost disappeared. In the finished leather, the only difference in appearance was a slightly lighter color in the bated half. Photomicrographs of exactly corresponding points on the grain surface of the two halves are shown in Fig. 85. The difference in appearance of the grain surface in the two cases is practically negligible. In carrying out practical tests of this kind, tanners usually fail to appreciate the importance of having the test pieces in equilibrium with solutions of

the same pH value and often attribute to differences in bating differences in the properties of the leather actually caused by differences in pH value.

While bated and unbated finished leathers appear much alike to the eye, there are perceptible physical differences, such as one might expect to find in view of the fact that the elastin fibers have been removed from under the grain of the bated leather. The desirability of completely, or even partially, removing elastin from skin depends upon the use to which the leather is to be put. Bated leathers are

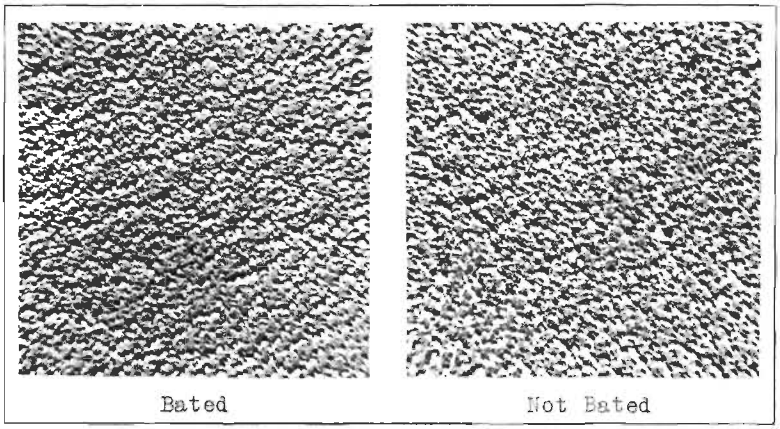


Fig. 85.—Grain Surfaces of Tanned Calf Skin.

Eyepiece: none. Wratten filter: K2-yellow.
Objective: 48-mm. Magnification: 7 diameters.

usually a little softer than unbated leathers, but this is desirable for some leathers and undesirable for others. Wood[24] believes that it is not necessary, or even desirable, to remove all of the elastin in bating, but that it is sufficient for the elastin fibers to be broken up or weakened, in order that the desired suppleness may be obtained.

Digestion of Collagen during Bating.

Although Thomas and Seymour-Jones have shown that pancreatin hydrolyzes collagen, the work of Wilson and Daub indicates that no serious loss of collagen occurs where the pH value is kept within the limits 7.5 to 8.0 and the action is stopped just as soon as all of the elastin fibers have been dissolved. Unduly prolonging the bating operation is sure to result in a very considerable hydrolysis of collagen, with corresponding decreases in the yield and firmness of the leather. Often an apparently heavy loss of collagen during

[24] The Properties and Action of Enzymes in Relation to Leather Manufacture. *Loc. cit.*

bating may be attributed to a previous breaking down of the collagen by excessive liming, putrefaction, or contact with liquors containing much ammonia. Manufacturers of glove leather sometimes make use of these agencies in order to get a very soft leather. They leave the skins in the lime liquor until a considerable amount of hydrolysis of collagen has taken place and then subject the skins to a prolonged bating. Much valuable collagen is thus lost, but the skins are thereby rendered more suitable for a specific purpose.

Chapter 10.

Drenching and Pickling.

In the final preparation of the skin for tanning, the pH value of the solution absorbed by the skin and with which the skin is in equilibrium must be adjusted to suit the particular method of tanning to be employed. During liming, this solution has a pH value of about 12.5; during bating, a pH value of about 7.5. Before skins can be tanned properly by any of the common methods of tanning, the pH value of this solution must be lowered considerably below the value 7.5. During vegetable tanning, the pH value of the liquor is usually less than 5 and in chrome tanning less than 4. By using tan liquors containing the proper excess of acid, the adjustment of pH value may be made in the tan liquor itself. But this is often a very difficult matter where the process is not under rigid chemical control.

Drenching.

For certain classes of leather, it is customary to subject the bated skins, before tanning, to a process known as *drenching*. Sometimes the bating process is omitted, as entirely unnecessary, and the skins are drenched directly after the washing following the unhairing process. The drench liquor is prepared by mixing 5 to 10 grams of bran per liter of water at 30° to 35° C. and allowing the mixture to ferment, with the formation of organic acids. The skins are put into this liquor contained in a vat equipped with a paddle wheel which keeps the liquor well stirred. In some tanneries, the fermentation is carried out in special tanks and only the clear, decanted, acid solution used on the skins. The acid dissolves any lime remaining in the skin and brings the skin into a more suitable condition for tanning. The particles of bran also exert a sort of cleansing action upon the skin, tending to absorb dirt and greases. The treatment is usually continued for several hours, but the completion of the process is determined by skilled workmen, who have learned to judge by the feel and appearance of the skin just when it is ready for the particular tanning process to be employed.

During the process, there is a considerable evolution of gas, which tends to cause the skins to float to the surface. In a drench in actual use, Wood [1] found that the gases had the following composition:

[1] The Properties and Action of Enzymes in Relation to Leather Manufacture. J. T. Wood. *J. Ind. Eng. Chem.* 13 (1921), 1135.

Carbon dioxide	25.2 per cent
Hydrogen sulfide	trace
Oxygen	2.5
Hydrogen	46.7
Nitrogen	26.0

The acids produced per liter were

Formic	0.0306 gram
Acetic	0.2042
Butyric	0.0134
Lactic	0.7907

Only an insignificant quantity of other materials were formed during drenching, trimethylamine being the chief.

It was found that the starch of the bran is converted into glucoses and dextrin by the action of an amylolytic enzyme, cerealin, discovered by Mege Mouriès.[2] It resembles the diastase of translocation described by Brown and Morris [3] in their work on the germination of grass seeds. It transforms starch into dextrin and glucose, whereas ordinary malt diastase transforms starch into dextrin and maltose. The action of cerealin is much slower than that of diastase. The sugars are then fermented by bacteria (*Bacillus furfuris*) with the formation of the organic acids listed above. The principal acid produced is lactic; the acetic acid is produced directly from the glucoses without any preliminary alcoholic fermentation by yeasts.

In the hands of experienced operators, the drenching process seldom gives much trouble, but it is not quite foolproof. If the acidity of the liquor increases rapidly and the skins are not removed in time, they become excessively swollen and may even be destroyed by hydrolysis, especially if the liquor is very warm. How much enzymes play a part in this hydrolysis is not yet known. Apparently danger from this source can be prevented by adding salt to the liquor to repress the swelling of the skin just as soon as it becomes very noticeable.

In his review of the damage to skins that may be caused by improper control of the drenching operation, Wood [4] points out that the discovery of the effectiveness of salt in preventing the destruction of skin in an acid liquor that would otherwise cause excessive swelling represents the origin of the modern pickling process.

Sometimes the fermentation may not proceed in the usual manner and the liquor, instead of becoming acid, turns slightly alkaline, frequently becoming bluish black, due to the presence of chromogenic bacteria. Under these conditions the skin is rapidly attacked by proteolytic organisms, but may be saved if transferred in time to a solution of acid and salt.

When the fermentation is accompanied by a very rapid evolution

[2] *Compt. rend.* 37 (1853), 351; 38 (1854), 505; 43 (1856), 1122; 48 (1859), 431; 50 (1860), 467.
[3] *J. Chem. Soc.* 57 (1890), 458.
[4] Puering, Bating and Drenching of Skins, p. 237.

of gas, the skins may be damaged by the formation of gases inside of the skin which burst out through the grain surface, leaving small holes. A damage very similar in appearance may be caused by proteolytic bacteria developing on the grain surface, each colony forming a small hole. This usually results from operating the drench at too high a temperature. A high temperature, especially in the presence of an excess of acid over that normally present, may result in a considerable amount of hydrolysis of collagen and the leather will feel rather spongy and empty.

When bacteria attack the grain during drenching, the surface of the finished leather may show dull patches, as though it were etched. In one instance, Eitner[5] found that this was caused by *Bacillus megaterium,* which formed a slimy film over the grain surface, which was attacked by a proteolytic enzyme secreted by the bacillus.

Wood and Wilcox[6] showed that if the acids ordinarily found in the drench are used in pure solution in the proportions in which they occur in the drench, the action upon the skin is the same, except for being more rapid. With the appreciation of the fact that the active constituent of the drench is the acid formed, tanners began to substitute pure solutions of organic acids, such as lactic and acetic. These could be used with safety, simply by adding the acid at such rate as to keep the solution just neutral to methyl orange. Hydrochloric acid, being cheaper, is often used, although it makes the control more delicate. In this way practically all of the lime can be removed from the skins and the skins then combine with a sufficient amount of the acid so that they do not reduce the acidity of the ordinary vegetable tan liquor into which they may be put.

But even when pure solutions of acid were employed to drench skins, no fixed rule could be made for all tanneries. If the vegetable tan liquors contained a considerable amount of salt and other soluble nontannins, the drench could be operated at a lower pH value with safety. Where fresh liquors of tanning materials containing a relatively small proportion of nontannin were used, there was danger of the skins being damaged by the rhythmic swelling described in Chapter 5, whenever the pH value of the drench fell below some fixed value, which depended upon the composition of the tan liquor employed. This trouble can be avoided by the addition of salt to the tan liquor, but the remedy may be almost as undesirable as the disease, since many tan liquors are precipitated by the addition of salt. In general, the purer the first tan liquor into which the skins are put after drenching, the more delicate must the control of the drenching operation be.

It sometimes happens that the tan liquors employed contain easily fermentable sugars, which are continually being converted into organic acids. In such cases, the use of a drench prior to tanning may be undesirable and even the bating operation may be unnecessary, where

[5] *Gerber* (1898), 204.
[6] Further Contribution on the Nature of Bran Fermentation. J. T. Wood and W. H. Wilcox. *J. Soc. Chem. Ind.* 12 (1893), 422.

the removal of elastin is not important. The tan liquor itself actually becomes a drench and the lime salts formed serve to prevent rhythmic swelling. Where the skins have been drenched prior to putting into the tan liquor, the acid present may prove excessive and the skins will be spoiled.

One tanner may employ a non-acid tan liquor preceded by a drench, another may use acid tan liquors and do away with the drenching operation, and yet both may produce the same kind of finished leather. But one would not dare to adopt only a part of the other's methods, which might prove disastrous; he must adopt all or none. This will serve to explain why it is not possible to outline quantitatively a rigid system of bating, drenching, deliming, or any other process, so that it may be used in any tannery. All fundamental operations in any one tannery are interdependent and a change, even one for the better, in one operation might necessitate a corresponding change in nearly every other operation.

Pickling.

The pickling operation differs from drenching chiefly in the fact that salt is used in conjunction with the acid. Formerly it was the customary practice to soak the limed or bated skins in a vat containing dilute sulfuric acid until they became somewhat swollen and then to transfer them to a saturated solution of sodium chloride, which repressed the swelling. Now it is more common to use the acid and salt in solution together, the preliminary swelling having been found unnecessary and sometimes undesirable. A satisfactory pickle liquor for most purposes consists merely of a molar solution of sodium chloride to which sulfuric acid is added in the desired amounts.

Pickle liquors are used for a number of different purposes, the chief of which are the preparation of skin for chrome tanning and the preservation of unhaired skins so that they may be kept for an indefinite period before tanning.

In preparing skins for chrome tanning, the concentration of acid most desirable to use depends upon the degree of basicity of the chrome liquor employed. The more concentrated the acid in the pickle liquor, the more quickly does the system tend to reach a condition approximating equilibrium. Furthermore, the more concentrated the acid solution absorbed by the skin, the more quickly will the chromium salts penetrate into the interior of the skin during the tannage. On the other hand, if the concentration of acid is too great, the rate of fixation of chromium by the skin will be reduced to an undesirable degree, unless the excess of acid is neutralized by the addition of sodium bicarbonate, borax, or other agent, during the tannage.

Pickling has the advantage over drenching that it is extremely easy to control chemically. If the concentration of salt is not allowed to fall below half-molar, the pickle liquor can be controlled by simple titrations, using methyl orange as indicator. Regardless of the variable amounts of lime which the skins may contain before pickling, they

can all be brought into a uniform condition simply by so regulating the concentration of acid that all skins finally reach equilibrium with solutions of the same concentration. When used in this way, the pickling process becomes a stabilizer of inestimable value in chrome tanning.

When the equilibrium concentration of acid is maintained at 0.05 normal or greater, the pickling of light skins requires only a few hours, but for weaker solutions and for heavy hides, the stock must remain in the liquor over night. In acid solutions greater than 0.01 normal, there is practically no danger of the skins being attacked by bacteria. The salt present is sufficient to prevent undue swelling at any pH value so that the process may be considered entirely safe, if only ordinary care is used.

For preserving skins, after bating, it is sufficient to bring them into equilibrium with a solution containing 1 mole of sodium chloride and 0.01 mole of sulfuric acid per liter. The liquors may be used for several consecutive lots of skin as the calcium sulfate formed is soluble in acid solution. The skins are usually pickled in vats equipped with paddle wheels, which keep the skins and liquor in motion, greatly hastening the attainment of equilibrium. After equilibrium has been established, the skins are withdrawn from the liquor and thrown over wooden horses to drain. They may then be kept in a damp condition for many months.

It is often desired to tan such skins later in vegetable tan liquors of such composition that they would be precipitated by the salt and acid present in the skins. In such cases, the skins are first depickled by soaking in paddle vats containing a solution of half-molar sodium chloride to which borax is added at such rate as to keep the solution neutral to methyl orange. When equilibrium has been established, the skins are transferred to a wash wheel and the salt washed out by means of running water. They are then ready for tanning. Depickling is unnecessary in the case of chrome tanning.

In the control of pickle liquors, it must not be assumed that the decrease in concentration of acid is caused only by its neutralization by lime. Two other factors contribute to the decrease. The bated skins usually contain about 80 per cent by weight of water, only 20 per cent representing collagen. Part of the decrease is caused by the dilution by this water. The author has found that 1 gram of collagen combines with approximately 0.00133 gram equivalent of acid. By making allowance for the decrease in concentration of acid caused by dilution and by combination with the collagen, the amount consumed in neutralizing lime can be roughly approximated.

Chapter II.

Vegetable Tanning Materials.

It has been known since prehistoric times that raw skin is colored and rendered imputrescible by contact with aqueous solutions of materials obtained from many forms of plant life. The active principle, which is widely distributed throughout the vegetable kingdom, is a class of complex organic compounds known as *tannin.* By vegetable tanning is meant the combination of tannin with the protein matter of skin to form leather.

Among the materials which have assumed commercial importance as a source of tannin for leather manufacture are barks, woods, leaves, twigs, fruits, pods, and roots. Tanning extracts obtained from different sources show very different properties, which is due in a large measure to the foreign matter extracted with the tannin.

Classification.

Many attempts have been made to classify tanning materials according to their behavior in tanning practice, but this varies so widely with the nature and proportions of foreign matters extracted with the tannin that attempts at classification on this basis have not yet resulted in any scheme of great practical value. The properties of a tanning extract depend more, in many cases, upon the method of extraction or the conditions under which it is used in the tannery than upon its source in nature. By suitably controlling the conditions of tanning, it has been found possible to get practically the same result from tanning materials otherwise exhibiting markedly different properties.

The tannins themselves, however, seem to fall chemically into two general classes, which have been named *pyrogallol* and *catechol* from the fact that tanning materials usually yield the one or the other of these two substances upon dry distillation. Upon fusion with sodium hydroxide, the pyrogallol tannins yield sodium gallate while the catechol tannins yield sodium protocatechuate. The pyrogallol tannins contain about 52 per cent of carbon as against about 60 per cent in the case of the catechol tannins. The two classes exhibit a number of different properties by which they may be differentiated.

All tannins seem to possess in common the property of precipitating gelatin from solution and this is used as a test to indicate the presence of tannin in solution. The reagent is made by dissolving 10

grams of gelatin and 100 grams of sodium chloride in 1 liter of water. One drop of the gelatin-salt reagent is added to 5 cubic centimeters of the solution suspected of containing tannin. Under ordinary conditions, a precipitate is formed if more than a trace of tannin is present. The sensitivity of this test and the conditions under which it may fail to operate will be discussed in Chapter 12.

When ferric salts are added to tannin solutions, a deep blue color is formed in the presence of pyrogallol tannins and a deep green in the presence of catechol tannins. All tannins are precipitated by lead acetate, but if the solution is first made approximately normal to acetic acid, the pyrogallol tannins only are precipitated by the addition of lead acetate, the catechol tannins remaining in solution. On the other hand, the catechol tannins are precipitated by the addition of an excess of bromine water, while the pyrogallol tannins remain in solution.

A common method for differentiating between pyrogallol tannins and those of the catechol group is to add 10 cubic centimeters of 40-per cent formaldehyde solution and 5 cubic centimeters of concentrated hydrochloric acid to 50 cubic centimeters of the tannin solution and to boil the mixture for half an hour in a flask fitted with a reflux condenser. Catechol tannins are completely precipitated by this treatment. The solution is cooled and filtered. To 10 cubic centimeters of the filtrate are added 5 grams of sodium acetate crystals and 1 cubic centimeter of a 1-per cent iron alum solution. A strong bluish violet coloration will appear if pyrogallol tannins are present, but none if the original solution contained only catechol tannins.

The separation of the tannins into these two groups and the extensive studies made of the reactions of the many different kinds of tanning materials have furnished the basis for a scheme of qualitative recognition of vegetable tanning materials which is sometimes of value in detecting adulteration in commercial tanning extracts. One of the best of these qualitative schemes is that of Procter.[1]

When liquors containing pyrogallol tannins undergo fermentation in the tan yard, they usually deposit finely divided ellagic acid, which appears as sludge in the bottom of the vat or as *bloom* on the surface of the leather. Catechol tannins, on the other hand, yield a difficultly soluble material called *reds*, or phlobaphenes.

Sources of Tanning Materials.

Only the more important raw materials will be mentioned here; for more comprehensive lists, the reader is referred to the standard work of Dekker[2] and to the books of Procter[3] and Harvey.[4] Among the barks used most widely as a source of tannin are those of the several varieties of oak. Oak bark is one of the few materials furnishing both pyrogallol and catechol tannins, although the latter predominate. Tan-

[1] Leather Chemists' Pocket-Book. H. R. Procter. E. & F. N. Spon, London (1912).
[2] Tanning Materials. J. Dekker. Verlang von Gebrüder Borntraeger, Berlin (1913).
[3] Principles of Leather Manufacture. H. R. Procter. D. Van Nostrand Co., New York (1922).
[4] Tanning Materials. A. Harvey. Crosby Lockwood & Son, London (1921).

ning extracts obtained from oak bark have long been favorites for the production of leather where firmness and solidity are desired. Hemlock bark is used extensively in the United States for the manufacture of heavy leathers. Extracts made from the barks of the larch, spruce, and fir are used to a very considerable extent both in America and in Europe. The barks of the mimosa, or wattle, the mallet, and the several species of mangrove, which are grown in Australia and South Africa, are very rich in tannin. Babool bark is commonly used in India and willow and birch in Russia. The leather known as Russia calf was originally tanned with birch bark, to which it owed its characteristic odor. As a general rule, the tannins of the barks belong to the catechol group.

Among the woods, that of the quebracho, grown in South America, is probably richest in tannin. The tannins of chestnut and oak woods find application in the manufacture of sole leather for blending with other materials. Quebracho tannin is of the catechol type, while that of chestnut and oak woods is of the pyrogallol type. The extract obtained from the cutch wood of India is widely used as a mordant in the dyeing of leather. Recently an extract of the wood of the osage orange tree has appeared on the market both as a natural dyestuff and as a tanning agent.

The most important extracts obtained from leaves and twigs are those of the gambier of India and the sumac of Sicily. The former belongs to the catechol and the latter to the pyrogallol group. Gambier is one of the mildest tanning materials known, a property which it apparently owes to the large amount of nontannins present in the extract. It is used as a mordant and, in mixtures with other materials, in the manufacture of light leathers. Sumac is commonly used to tan the grain splits of sheep skins for hat bands, etc., and as a mordant. It is rather easily decomposed by boiling water.

A variety of unripe nuts and pods form a much used source of tannin, usually of the pyrogallol type. These often contain easily fermentable sugars and, by their use in tanning, it is often possible to do away with the acid *drench* to which skins are sometimes subjected prior to tanning. The light colors obtained when using materials like these, which yield acids by fermentation, may be explained, in the light of recent investigations, by the fact that the color of a tan liquor as well as that of the leather it produces becomes lighter the lower the pH value. The pods of the algarobilla and divi-divi, grown extensively in Central and South America, and the dried, unripe nuts of the myrobalan tree of India are used in mixtures with other materials that do not yield acids so readily. In the preparation of some mixtures, valonia, from the acorn cups of the Turkish oak, is favored. Another easily fermentable tanning extract is obtained from the babool pods of India, which contain both pyrogallol and catechol tannins.

Among the roots used as a source of tanning extracts, those of the palmetto, grown in the United States, and the canaigre, grown in Mexico and Australia, are perhaps the most common. The latter is rich in catechol tannin and has a tendency to ferment rather easily.

Where there is no chemical control of the tan liquors, the selection of tanning materials must be governed by the nature of the operations preceding and following the tanning process, as well as by price and availability of the materials. While quebracho extract, for example, is an excellent tanning material, its pure solutions are hardly suitable for receiving consecutive lots of raw skin containing much lime. Their naturally low acidity would be quickly neutralized and the tannin would then be precipitated by the lime, or oxidized, and cease to tan properly. But this danger would be greatly lessened by the use of a mixture of tanning extracts containing acid-producing materials, like those in divi-divi or myrobalans.

Leaching.

It is still common to find tanneries equipped to extract the tannin from the raw materials grown in neighboring districts, although the manufacture of tanning extracts has now become a separate industry, which has proved useful in making a greater variety of materials available to the individual tannery.

One of the oldest systems for leaching raw materials, and the one most commonly used in tanneries, is known as the open vat method. The bark, or other material, is broken into small pieces and then shredded in a bark mill. The leaching tanks are usually arranged in batteries of about eight and are fitted with perforated false bottoms on which the bark is placed. The bottom of each tank is fitted with a pipe through which liquor may be drawn off or pumped from one tank to another. When fresh bark is put into a given tank, liquor is run onto it which has been used to leach the bark in all of the seven other tanks. This strong liquor is finally drawn off and pumped into a storage tank. The bark is then leached with liquor which has passed through only six other tanks. The eighth leaching of this bark is made with fresh water, after which the bark is dumped and discarded.

Fresh water is used to leach only the most nearly exhausted bark. As the liquor becomes stronger in tannin, it is run onto fresher bark, and finally onto the previously unleached bark. As soon as each tank is dumped, it is again filled with fresh bark and becomes the head vat in the cycle, which is continuous. The object of this system of leaching is to get final liquors as concentrated as possible. In the tannery, the liquor in the storage tank is used as needed, but in the extract plant it is necessary to evaporate off most of the water so as to make its subsequent transportation practical.

The extraction of the raw material is often facilitated by the use of mechanical devices. Sometimes the leaching tanks are equipped with mechanical stirrers or with pipes for bubbling air up through the liquor. In another system, the tanks are replaced by revolving drums, used on the same principle as the open vats, the liquor being pumped from one drum to another. In still another system, the bark, or other material, is forced through a trough in one direction, by means of a screw conveyor, while water flows over the bark in the

opposite direction. At the point of entry of the fresh water, the bark is practically exhausted and is dumped onto a pile from which it is subsequently moved to the furnaces for fuel, or is disposed of in some other way. At the point of entry of the bark, the liquor is richest in tannin and is conducted to the storage tank.

In many extract plants, autoclaves are employed in order to leach the bark under pressure, which increases the yield obtained. The liquor is pumped from one autoclave to another, just as in the open vat system. In a system only recently devised, the raw materials are leached in autoclaves under a vacuum. The advantage claimed for this is that the liquor may be kept boiling at a very low temperature, giving increased yields, but not at the expense of the quality of the extract. The relative merits of the pressure and vacuum systems will probably be brought out more clearly when they have been more thoroughly investigated.

Effect of Temperature.

The rate at which tannin can be extracted from the raw material increases with the temperature of the water used, but so also does the rate at which the dissolved matter decomposes. The variation of the ratio of these two rates with temperature determines the optimum temperature that it is desirable to employ and this is different for different materials. It is customary to extract the fresh material at a low temperature and to increase the temperature of extraction until the material is practically exhausted. In using the open vat system for ordinary barks, it is a good plan to have the fresh water at the boiling point and to allow its temperature to fall slowly to about 60° C. as it passes over fresher bark. The temperature of the liquors can be controlled by having suitable heating coils placed in the tanks just under the false bottoms.

Effect of Hardness and Alkalinity of the Water.

When a very hard, alkaline water is used in leaching, the tannin yield is very low and the extract is dark in color and of poor quality. This has been the subject of numerous investigations, from which the general conclusion has been drawn that the use of a soft water in leaching is imperative. But the recent work of Wilson and Kern seems to indicate that the question of hardness of the water used is of less importance than the pH value of water and liquor.

Effect of pH Value on the Color of Tan Liquors.

Wilson and Kern [5] made a special study of the effect of pH value on the color of gambier and quebracho liquors. Two tan liquors were prepared, one from gambier and the other from quebracho extract. To

[5] The Color Value of a Tan Liquor as a Function of the Hydrogen-Ion Concentration. J. A. Wilson and E. J. Kern. *J. Ind. Eng. Chem.* 13 (1921), 1025.

each was added sufficient phosphoric acid to bring the pH value to 2.5, as determined by the hydrogen electrode. The phosphoric acid was added to act as a buffer in preventing large changes in pH value upon long standing. To equal portions of each, sodium hydroxide was added to give series of tan liquors ranging in pH value from 3.0 to 12.0 and all having a tannin content of 1 per cent, as determined by the Wilson-Kern method, to be described in the next chapter. The gambier series varied in color from light straw at 3.0 to a very deep red at 12.0. The quebracho series was similar in color excepting that the liquors of lower pH value had a touch of violet. Either series suggested a standard series of colors such as is used in the indicator method of determining hydrogen-ion concentration, except for the fact that a light precipitate formed in all liquors having a pH value of 4.0 or less. The difference in color was evidently a true indicator effect, for any member of one series could be made to match any other member simply by bringing it to the same pH value. All members of either series appeared practically identical when brought to a pH value of 3.0. This complete reversibility of color change, however, was not found when liquors at higher pH values were allowed to stand long exposed to air.

Effect of pH Value on the Oxidation of Tan Liquors.

Two complete series of each extract were poured into test tubes; the tubes of one series of each were tightly stoppered, while the others were left open to the air. Next day the liquors in the stoppered tubes showed practically no change, but the others had become darker in color, the more so the higher the pH value. When the liquors in a series not exposed to air were all brought to a pH value of 3.0, they all assumed practically the same color. But when those of a series that had been exposed to air were all brought to 3.0, they did not assume the same color, but were darker the higher the pH value during the period of exposure to air; furthermore a precipitate settled out from those whose pH values had been in the vicinity of 9.

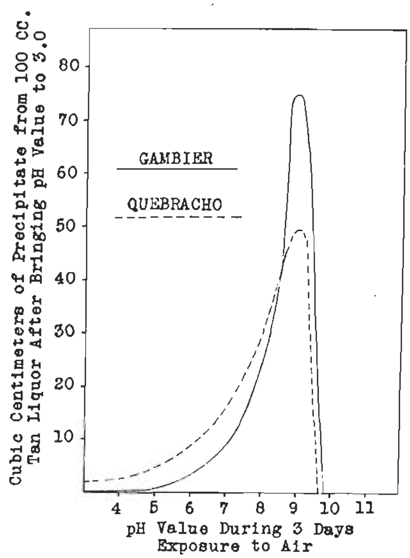


FIG. 86.—Showing how tendency of a tan liquor to form a precipitate when brought to a pH value of 3 varies with its pH value during a period of exposure to air.

This precipitate formation is very curious. A complete series of each extract was allowed to stand exposed to air in shallow dishes for 3 days; the liquors were then made up to original volume and poured

into 100-cubic centimeter graduate cylinders. Each was brought to a pH value of 3.0 by the addition of hydrochloric acid and allowed to stand over night. Next day the volume of precipitate from 100 cubic centimeters of original liquor was read from each cylinder. The results are shown in Fig. 86.

Keeping a solution of either extract exposed to air while its pH value is 9 causes it to yield an enormous precipitate when its pH value is subsequently brought to 3.0. But keeping it exposed to air when its pH value is greater than 10 apparently prevents its precipitation when brought to 3; all such liquors remained brilliantly clear. The addition of a great excess of acid, however, caused all liquors to precipitate, while any precipitate could be completely redissolved by the addition of sufficient alkali.

Another interesting fact is that the liquors exposed to air when their pH values lay between 8 and 9 gave much trouble with the hydrogen electrode. After bubbling hydrogen through them for only a few minutes, the voltage would fall rapidly towards zero. Even when brought to a pH value of 3.0, the liquors still gave this trouble, making it necessary to check the results by means of indicators. No such trouble was encountered with liquors exposed to air at pH values below 7 or above 10. Apparently $pH = 9$ is a critical point in the oxidation of tan liquors.

The curves in Fig. 86 show that this effect of oxidation is appreciable at all pH values from 6 to about 10. Most hard waters have pH values lying within this range and many of them have pH values higher than 8.

Effect of pH Value on the Precipitation of Tan Liquors.

Wilson and Kern [6] also studied the effect of pH value on the precipitation of quebracho liquors. Four series of solutions of solid quebracho extract were prepared according to the official method of the American Leather Chemists Association,[7] except for the additions of sulfuric acid, hydrochloric acid, sodium hydroxide, and calcium hydroxide, respectively, to the four series to produce approximately the desired pH value before making each solution up to the required volume. The pH values were finally determined at 20° C. by means of the hydrogen electrode and the solutions were analyzed according to the official method. The effect of the added acid or alkali upon the per cent of insoluble matter found is shown in Fig. 87.

The solution receiving no addition of acid or alkali had a pH value of 4.60. As the pH value was lowered from this, by the addition of either sulfuric or hydrochloric acid, there was an increase in the per cent of insoluble matter found, sulfuric acid proving the more effective in causing precipitation. With increasing pH value, there

[6] Effect of Hydrogen-Ion Concentration upon the Analysis of Vegetable Tanning Materials. J. A. Wilson and E. J. Kern. *J. Ind. Eng. Chem.* 14 (1922), 1128.
[7] *J. Am. Leather Chem. Assoc.* 16 (1921), 113.

first a decrease in the amount of insoluble matter and the un-red solution gradually became more nearly transparent. In the of the liquors containing sodium hydroxide, this continued with-a break, the liquor having a pH .e of 11.35 being quite trans-:nt. But at the neutral point, an ıpt change occurred in the solu-s containing calcium hydroxide; ı further rise in pH value, the .in was precipitated in increasing unts.

[f these data may be applied ıtitatively to raw tanning ma-ıls in general, it is evident that precipitation of tannin by lime be prevented by keeping the value of water and liquor, dur-extraction, under 7. But to d appreciable oxidation effects, material should not be ex-ted at pH values greater than hich may be accepted tentatively ıe optimum pH value for leach-since, with decreasing values, e is an increasing amount of ɜrial precipitated. Where only l water is available for leaching, ɔuld seem the part of wisdom to add to it, before using, a sufficient ıtity of acid to lower its pH value to 5.

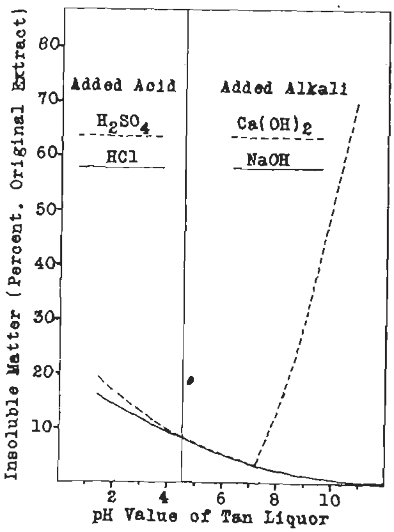


Fig. 87.—Effect of pH value on per cent of insoluble matter in solution of quebracho extract.

Clarifying, Decolorizing and Drying.

ı the manufacture of tanning extracts for sale, it is desirable the extract should be clear, have a good color, and be dried to ·gree sufficient to make handling and shipment easy. Clarifica-which consists merely of the removal of finely divided matter ıspension, is effected by settling and decantation, by filter-pressing, ›y centrifuging.

Vhere the extract manufacturer has carried the extraction of the material nearly to the limit, the extract is apt to have a dark ·, which is not desirable. This seems to be due to the extraction ɔreign matters at the high temperatures used, or, in some cases to ation. A common method of clarifying and decolorizing some ex-s is by means of blood albumin. The tan liquor is treated with lution of blood albumin and then heated to a temperature of C., at which the albumin coagulates and carries down with it the ɜnded matters, some of the deeply colored bodies, and some tannin. clear liquor is decanted off and the sludge is filter-pressed to re-

cover the adhering tan liquor. Although some tannin is lost in this way, the color of the extract is greatly improved.

A number of other methods of decolorizing involve the treatment of the tan liquor with chemicals. Sulfur dioxide and sodium bisulfite are often used. Some brightening of the color would naturally be expected from the lowering of the pH value of the liquor by sulfur dioxide, but the total effect seems to be more complex than this, since some of the suspended and difficultly soluble matters are thereby rendered soluble. Apparently the reducing action of sulfur dioxide plays a part.

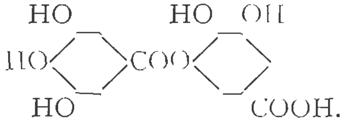
There are naturally numerous methods in use for drying extracts. Since high temperatures and contact with the air during drying are undesirable, much of the drying is done in specially constructed vacuum dryers. As these have been greatly improved, from time to time, it has become possible to dry extracts to greater extents without causing them to suffer any damage. Formerly it was customary to reduce the water content of most extracts only to from 50 to 60 per cent, but now it is not uncommon to find extracts on the market having a water content as low as 10 per cent.

Chapter 12.

The Tannins.

Some idea of the volume of literature which has appeared dealing with the composition of tanning materials may be gained from the bibliography, compiled by Dean,[1] of the more important papers published prior to 1910, which lists 273 papers. It is remarkable that the greatest work on the organic chemistry of the tannins was accomplished by the same man who did most to elucidate the complex structure of the proteins, Emil Fischer. Among the numerous papers by Fischer and his coworkers, telling of their work which led to the discovery of the composition of tannin, may be mentioned one entitled "Synthesis of Depsides, Lichen-Substances and Tannins," [2] which is something in the nature of a review. The tannin studied by Fischer was that obtained from nutgalls, the so-called gallotannic acid and purest form of pyrogallol tannin.

As early as 1852, Strecker [3] concluded that tannin was a compound of glucose and gallic acid. He was supported by the works of van Tieghem,[4] who found glucose among the hydrolytic products of tannin, and Pottevin,[5] who effected the hydrolysis with the enzyme of *Aspergillus niger*. But the variation in proportion of glucose found weakened the view, which gave way to that of Schiff,[6] who regarded tannin as digallic acid:



Although Schiff's formula for tannin was widely accepted, it was shown very definitely that digallic acid is not tannin. The formula showed no asymmetric carbon atom in the molecule to account for the optical activity of the natural tannin and it could not account for the high molecular weights observed. By observing the electrical conductivity, light absorption, and behavior towards arsenic acid, Walden [7] showed that Schiff's digallic acid is very different from natural tannin.

Fischer and Freudenberg [8] first set out to determine whether the

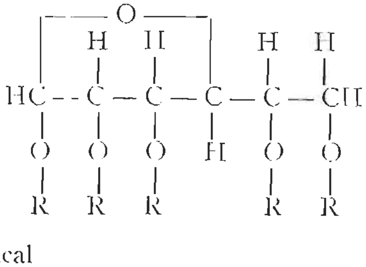
[1] On the Composition of Tanning Materials; Bibliography 1828-1909. A. L. Dean. *J. Am. Leather Chem. Assoc.* 6 (1911), 172.
[2] Emil Fischer. *Ber.* 46 (1913), 3253. *J. Am. Chem. Soc.* 36 (1914), 1170.
[3] A. Strecker. *Ann.* 81 (1852), 248; 90 (1854), 328.
[4] P. van Tieghem. *Annal. d. Sciences naturelles V. Serie Botanique* (1867), 210.
[5] H. Pottevin. *Compt. rend.* 132 (1901), 704.
[6] H. Schiff. *Ber.* 4 (1871) 232, 967; 12 (1879), 33.
[7] P. Walden. *Ber.* 30 (1897), 3151; 31 (1898), 3167.
[8] E. Fischer and K. Freudenberg. *Ber.* 45 (1912), 919.

glucose found by Strecker was really a constituent or only a chance impurity of tannin. They started with the purest technical tannin available. Assuming that the tannin molecule had no carboxyl group, they proceeded to separate it from acid impurities by rendering its solution slightly alkaline and extracting it with ethyl acetate, a method discovered independently and published previously by Paniker and Stiasny.[9] As they had anticipated, the tannin dissolved in the ethyl acetate, leaving the sodium gallate in the aqueous solution. They accepted this as proof that the tannin possessed no free carboxyl group. Applying this method of purification to different kinds of commercial tannin, they obtained products that were practically identical.

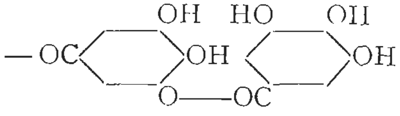
After hydrolyzing the purified tannin with sulfuric acid, they found between 7 and 8 per cent of glucose. In the purest sample of tannin examined, they found one molecule of glucose combined with ten molecules of gallic acid. No phenolcarboxylic acid other than gallic could be found in tannin, even when the hydrolysis was effected by means of alkali. With excess of alkali and exclusion of air, large yields of alkali salt of gallic acid were obtained in relatively pure condition.

It appeared to Fischer that the surest way to prove his assumptions regarding the structure of tannin was to synthesize it. He started out with the idea that tannin contains no carboxyl and that, consequently, the gallic acid must all be bound as an ester, a condition that would be fulfilled by regarding tannin as an ester-like combination of one molecule of glucose with five molecules of digallic acid, after the manner of pentacetyl glucose.

The investigations of Fischer and his collaborators are so extensive as to require treatment in a separate volume and the reader is referred to the recent book by Freudenberg,[10] who is continuing Fischer's work on the tannins. Fischer [11] succeeded in preparing penta-*m*-digalloyl-β-glucose, which was proved to be an isomer of the tannin from Chinese nutgalls. The formula for the so-called gallotannic acid may thus be written



where R is the radical



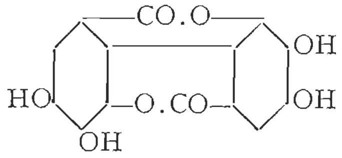
[9] *J. Chem. Soc.* 99 (1911), 1819.
[10] Die Chemie der Natürlichen Gerbstoffe. K. Freudenberg. J. Springer, Berlin (1920).
[11] E. Fischer and M. Bergmann. *Ber.* 51 (1918), 1760.

Freudenberg has suggested a classification of the tannins more distinctive than the catechol-pyrogallol system mentioned in Chapter 11. He would divide them into two main classes, the first consisting of hydrolyzable tannins in which the benzene nuclei are united to larger complexes through oxygen atoms, and the second of condensed tannins, in which the nuclei are held together through carbon linkages. Where both kinds of compounds are present, as in ellagic acid, the classification is decided by the genetic connection with other tannins.

The first group embraces three classes: (1) depsides, esters of phenolycarboxylic acids with each other or with other oxyacids; (2) the tannin class, or esters of phenolcarboxylic acids with polyatomic alcohols and sugars; and (3) glucosides. The most important criterion of the first group is hydrolysis to simple components by enzymes, particularly tannase or emulsin. Freudenberg and Vollbrecht[12] have recently discussed the isolation and determination of the activity of tannase, which is secreted by *Aspergillus niger.*

The second group of tannins are not decomposed to simple components by enzymes. They are generally, but not always, precipitable by bromine and condense to amorphous tannins, or *reds,* of high molecular weight, when treated with oxidizing agents or with strong acids. They are divided into two classes according to whether or not phloroglucin is present. With the exception of some simpler ketones, oxybenzophenones and oxyphenylstyrylketones, the catechins belong to the phloroglucin class, which include the tannins of quebracho and probably also those of oak bark.

That the reds, or phlobaphenes, precipitated by acid from solutions of quebracho and gambier extracts are oxidation products is indicated by the curves in Fig. 86, which show that the quantity of precipitate obtained is greatly increased by previous oxidation. The actual composition of the phlobaphenes is not yet known. The ellagic acid, or *bloom,* formed in solutions of tanning extracts of the pyrogallol group, is of very much simpler composition than the phlobaphenes. The formula



for ellagic acid, suggested by Graeb,[13] is the most satisfactory thus far proposed.

Practical Definition of Tannin.

The great classical work on the structure of the tannins is still too far from complete to enable one to apply organic chemistry to practical tanning, excepting, perhaps, in the study of the reactions

[12] *Z. physiol. Chem.* 116 (1921), 277.
[13] *Chem. Ztg.* (1903), 129.

of particular groups present in the tannin molecules. The structures of the tannins of the catechol group are still entirely unknown. As in the case of the proteins, it has been found necessary to deal with the general properties of the tannins from the standpoint of physical rather than organic chemistry.

All tannins seem to have the property of precipitating gelatin from solution and of combining with the protein matter of hide fibers, forming a compound resistant to washing. Any natural vegetable material having this property in aqueous solution has generally been accepted as tannin, and this has been made the basis for the various methods of determining tannin now in use. The portion of soluble matter which neither combines with collagen to form a compound resistant to washing nor precipitates gelatin from solution is known as nontannin.

The Gelatin-Salt Test for Tannin.

In testing a solution for the presence of tannin, it is customary to add to it one drop of a solution made by dissolving 10 grams of gelatin and 100 grams of sodium chloride in a liter of water, a precipitate or turbidity indicating the presence of tannin. This reaction has been the subject of numerous investigations for more than a century. Its sensitivity as a means of detecting tannin in solution has recently been studied by Thomas and Frieden.[14] They found that the added gelatin is completely precipitated when the ratio of gelatin to tannin does not exceed 0.5; a great excess of gelatin prevents precipitation.

Thomas and Frieden studied the precipitation of tannin by gelatin at different pH values and concentrations of salt. Using a gelatin solution containing no salt, they obtained a maximum precipitation of gallotannic acid, in pure solution, at a pH value of 4.4; at pH values below 4 or above 5, the solutions became opalescent, but no precipitate formed. The effect of adding sodium chloride was to widen the range of pH value over which a precipitate was obtainable; it apparently had no effect upon the sensitivity of the test between the pH values 4 and 5. Using various commercial tanning extracts, they found that the optimum range for precipitation of tannin by gelatin varied from 3.5 to 4.5, quebracho, wattle, and hemlock precipitating most readily at pH values slightly above 4.0 and gambier, oak, and larch at values slightly below 4.0.

The limits of dilution at which tannin could be detected by means of the gelatin-salt reagent were found to depend upon the proximity of the solution to the optimum pH value for precipitation, which is different for each kind of extract, but apparently always lies between 3.5 and 4.5. At the optimum pH value, gambier, the least sensitive to the test, could be detected at a concentration of 1 part of tannin to 110,000 parts of water. Wattle, the other extreme, could be detected at a dilution of 1 to 200,000. When the commercial extracts

[14] The Gelatin-Tannin Reaction. A. W. Thomas and A. Frieden. *Ind. Eng. Chem.* (1923); (advance copy).

were simply diluted with distilled water, no attention being paid to the final pH values, the sensitivity of the tests was greatly decreased. The least sensitive was then hemlock at 1 part in 6,500 and the most sensitive was gambier at 1 part in 30,000. They also found that the age of the gelatin-salt reagent has no effect on the sensitivity of the test, provided bacterial action is prevented by means of toluene.

The Determination of Tannin.

Although a general discussion of analytic methods is outside the scope of this book, the question of determining tannin demands some attention here because of its importance in leather chemistry and the fact that the methods in common use do not determine the actual tannin content of tanning materials, but include as tannin a variable fraction of nontannin, which, in the extreme case of gambier, is twice as great as the tannin content itself.

For more than a century leather chemists have struggled with the question of determining tannin and numerous methods have been proposed. Of these, the only one which has really survived is that known as the hide powder method. But even this is used in different parts of the world with different modifications. For a review of the various methods proposed up to 1908, the reader is referred to Procter's book.[15] It will serve our purpose here to give an outline of the official method of the American Leather Chemists Association, which is similar in principle, although not in all details, to those employed in various parts of Europe.

A. L. C. A. Method[16]

"American Standard" hide powder is specially prepared by giving it a light tannage with chrome alum, washing it practically free from soluble matter, and squeezing it until it contains not less than 71 nor more than 74 per cent of water. The solution of tanning material for analysis must contain not less than 0.375 nor more than 0.425 gram of tannin per 100 cubic centimeters, as found by this method. To 200 cubic centimeters of this solution is added such an amount of the wet hide powder as contains not less than 12.2 nor more than 12.8 grams of dry hide powder and the whole is shaken for 10 minutes. The detannized solution is separated from the powder by squeezing through linen and is then filtered through paper, after the addition of kaolin, the solution being returned to the paper until the filtrate is quite clear. The amount of residue from an aliquot portion of this filtrate, after correcting for the water introduced by the hide powder, is taken as a measure of the nontannin in the original material. The difference between the total soluble matter and the nontannin is called

[15] Leather Industries Laboratory Book. H. R. Procter. E. & F. N. Spon, London (1908).
[16] For further details, see *J. Am. Leather Chem. Assoc.* 16 (1921), 113.

tannin. The other determinations of the method need not concern us here.

It will be apparent from the discussion of the equilibria of protein systems in Chapter 5 that the method involves two false assumptions: one that the hide powder combines only with tannin; the other that the solution absorbed by the collagen jelly has the same concentration as that in the surrounding solution. It may be mentioned that the former assumption introduces errors vastly greater than the latter. As long ago as 1903, Procter and Blockey[17] showed

TABLE XVII.

RESULTS OF TREATMENT OF PURE GALLIC ACID SOLUTIONS BY A. L. C. A. METHOD.

(Using 47 grams of wet hide powder (73 per cent water) to 200 c.c. of solution.)

Gallic Acid Grams per liter	Nontannin Per cent	Tannin Per cent
8.88	54.0	46.0
4.44	47.1	52.9
2.22	43.8	56.2
1.11	40.4	59.6

TABLE XVIII.

EFFECT OF ALTERING PROPORTION OF HIDE POWDER UPON AMOUNT OF GALLIC ACID REMOVED FROM A 0.888-PER CENT SOLUTION.

(Using principle of A. L. C. A. method.)

Wet Hide Powder (73 per cent water) Grams per 200 c.c.	Nontannin Per cent	Tannin Per cent
5	91.8	8.2
10	86.0	14.0
25	69.6	30.4
50	52.1	47.9
75	43.7	56.3

that hide powder removes from solution considerable amounts of such nontannins as gallic acid, quinol, and catechol. Wilson and Kern[18] showed this even more strikingly by subjecting pure solutions of gallic acid to the A.L.C.A. method of tannin analysis. By varying the concentration or the proportion of hide powder, practically any results desired could be obtained. Tables XVII and XVIII show that the A.L.C.A. value for tannin decreases with increasing concentration of the solution and increases with the proportion of hide powder. Using a solution of 1 gram of gallic acid per liter, the method indicates a tannin content for the sample of about 60 per cent, even though it contains none at all.

[17] Absorption of Non-Tanning Substances by Hide Powder and Its Influence on the Estimation of Tannin. H. R. Procter and F. A. Blockey. *J. Soc. Chem. Ind.* 22 (1903), 482.

[18] The Nontannin Enigma. J. A. Wilson and E. J. Kern. *J. Am. Leather Chem. Assoc.* 13 (1918), 429.

Wilson-Kern Method.

With the object of avoiding the palpable errors of the A.L.C.A. method, Wilson and Kern [19] set out to devise a method that would determine exactly what is called for in the practical definition of tannin, namely, that portion of the soluble matter of vegetable tanning materials which will precipitate gelatin from solution and which will form compounds with hide fiber which are resistant to washing. The principle of their method is to shake a convenient amount of the tannin solution with a known quantity of purified hide powder until all tannin has been removed from solution, as determined by the gelatin-salt test. The tanned powder is then washed free from soluble matter including the nontannin removed from solution by the hide powder, which is responsible for the large errors in the A.L.C.A. method. It is then carefully dried and analyzed for tannin as in the regular procedure for vegetable-tanned leathers, and from this figure the per cent of tannin in the original material may readily be calculated.

In order to show the workability of this method, Wilson and Kern selected 8 typical tanning materials showing great differences in properties, especially in so-called astringency. The solid quebracho extract and the four liquid extracts of oak bark, larch bark, chestnut wood, and osage orange are typical samples of the best of these materials on the American market. The gambier is the ordinary pasty product from the East Indies; the sumac, consisting of ground leaves and small twigs, is from Palermo; and the hemlock bark came from the forests of Wisconsin. The extracts were simply dissolved in hot water, cooled slowly, and made up to the mark. The bark and sumac were finely ground and leached by percolation, only the extracted portions being used after making up to a definite volume. In each test, 12 grams of hide powder (of known hide substance content) were put into a wide-mouthed, rubber-stoppered, half-pint bottle, the tanning material dissolved in 200 cubic centimeters of solution was added, and the whole was shaken in a rotating box for 6 hours.

The amount of material that could be used was limited by the amount of tannin that the hide powder was capable of taking up in 6 hours. On the other hand it was desirable not to use too little, since the less the amount of tannin fixed per unit of hide substance, the less the accuracy of the method, since the tannin was determined by difference. Whenever the liquor, after the 6-hour shaking, gave a turbidity or precipitate with the gelatin-salt reagent, the test was repeated with less material.

The tanned powder was washed by shaking with 200 cubic centimeters of water for 30 minutes, squeezing through linen, and repeating the washing operation until the wash water showed no color and gave no test with ferric chloride solution. Nontannins like gallic acid give a dark coloration upon the addition of ferric chloride solution. Except for the osage orange and chestnut wood extracts, which

[19] The True Tanning Value of Vegetable Tanning Materials. J. A. Wilson and E. J. Kern. *J. Ind. Eng. Chem.* 12 (1920), 465.

TABLE XIX.

Material	Material grams per Liter	Percentage Analysis of Tanned Hide Powder: Water	Ash	Fat	Hide Substance (N x 5.62)	Tannin (by difference)	Per 100 g. of Hide Substance: Tannin found Grams	Material used Grams	Tannin in Material Per cent
Quebracho	18.8	11.56	0.14	0.35	74.92	13.03	17.39	36.8	47.26
Quebracho	18.8	11.42	0.08	0.35	75.05	13.10	17.46	36.8	47.45
Quebracho	11.5	13.81	0.03	0.30	77.53	8.33	10.74	22.6	47.52
Hemlock Bark	150.0	9.94	0.12	0.24	76.54	13.16	17.19	287.9	5.97
Hemlock Bark	100.0	10.73	0.13	0.28	79.39	9.47	11.93	191.9	6.22
Hemlock Bark	75.0	12.76	0.05	0.28	79.53	7.38	9.28	147.1	6.31
Oak Bark	67.5	12.54	0.07	0.12	74.76	12.51	16.73	131.6	12.71
Oak Bark	45.0	11.19	0.09	0.24	79.36	9.12	11.49	87.6	13.12
Oak Bark	25.0	13.53	0.05	0.34	81.00	5.08	6.27	48.9	12.82
Larch Bark	67.5	12.59	0.09	0.13	75.61	11.58	15.32	131.6	11.64
Larch Bark	45.0	13.65	0.09	0.30	77.90	8.06	10.35	87.7	11.80
Larch Bark	25.0	16.52	0.08	0.25	78.65	4.50	5.72	48.9	11.70
Chestnut Wood	67.5	12.43	0.11	0.05	75.76	11.65	15.38	131.6	11.69
Chestnut Wood	45.0	12.82	0.13	0.19	78.54	8.32	10.59	87.7	12.08
Chestnut Wood	37.5	12.05	0.10	0.21	80.74	6.90	8.55	71.7	11.92
Sumac	93.8	11.39	0.16	0.36	74.92	13.17	17.58	179.3	9.80
Sumac	62.5	12.26	0.23	0.31	78.38	8.82	11.25	119.5	9.41
Sumac	37.5	11.75	0.12	0.37	81.97	5.79	7.06	73.5	9.61
Osage Orange	48.8	12.82	0.13	0.17	77.35	9.53	12.32	95.0	12.97
Osage Orange	32.5	12.83	0.09	0.25	80.09	6.74	8.42	63.3	13.30
Osage Orange	26.3	12.43	0.12	0.25	81.43	5.77	7.09	51.2	13.85
Gambier	50.0	12.08	0.18	0.19	81.44	6.11	7.50	97.4	7.70
Gambier	49.5	11.77	0.26	0.28	81.70	5.99	7.33	94.7	7.74
Gambier	29.0	13.06	0.14	0.35	82.74	3.71	4.48	56.5	7.93

are unusual in several respects, not more than 12 washings were required to free the powders from nontannin, which shows that the line of demarcation between tannin and nontannin is fairly sharp for the commoner materials. The wash water continued to extract coloring matter from the powders tanned with osage orange until after the fiftieth washing, while as many as 25 washings were required to free the powders tanned with chestnut wood from soluble matter producing a dark color with ferric chloride. All wash water was tested with the gelatin-salt reagent, but in every case the test was negative.

The washed powders were dried at room temperature for 24 hours or longer and then analyzed for water, ash, fat and hide substance. The per cent of hide substance was taken as the per cent of nitrogen multiplied by 5.62. The difference between 100 and the sum of the percentages of water, ash, fat and hide substance was taken as the per cent of tannin in the tanned powder. The parts of tannin per 100 parts of hide substance divided by the parts of tanning material used per part of hide substance gave the per cent of tannin in the original material. The results for the 8 materials examined are given in triplicate in Table XIX.

Comparison of A. L. C. A. and Wilson-Kern Methods.

The two methods just described give very different results. A careful comparison is therefore desirable, especially since it will assist in giving a better understanding of the vegetable tanning process and of what is ordinarily called tannin. It should be remembered that the great majority of tannin values quoted in the literature were obtained either by the A.L.C.A. method or by some method based upon similar principles. The Wilson-Kern method is still too new to have found general acceptance.

TABLE XX.

	Percentage Analysis of Material					
		A. L. C. A. Method			Wilson-Kern Method	Percentage Error in A.L.C.A
		Insoluble	Soluble Matter			
Material	Water	Matter	Nontannin	Tannin	Tannin	Method
Quebracho	17.87	7.16	6.96	68.01	47.41	43
Hemlock Bark	8.90	74.33	6.71	10.06	6.17	63
Oak Bark	52.66	3.68	19.46	24.20	12.88	88
Larch Bark	51.08	5.88	20.90	22.14	11.71	89
Chestnut Wood	58.90	1.50	13.80	25.80	11.90	117
Sumac	9.25	47.20	17.99	25.56	9.61	166
Osage Orange	46.05	3.45	10.63	39.87	13.37	198
Gambier	51.12	5.36	18.57	24.95	7.79	220

For the sake of comparison, Wilson and Kern analyzed the 8 materials they studied by both methods and the results are given in Table XX. The percentage error in the A.L.C.A. method is calculated on the assumption that the results of the Wilson-Kern method are correct. Although the enormous errors in the A.L.C.A. method

TABLE XXI.

EFFECT OF VARIATION IN AMOUNT OF HIDE POWDER USED UPON PER CENT OF TANNIN OBTAINED BY A. L. C. A. METHOD.

Material	Grams per Liter	Wet Hide Powder (73 per cent water) Used to Detannize 200 cc. Tan Liquor Grams	Apparent Per cent of Tannin by A. L. C. A. Method	Percentage Error Due to A. L. C. A. Method
Quebracho	3	93.3	68.18	44
		46.7	67.56	43
		26.7	66.61	40
		13.3	64.36	36
		6.7	57.56	21
Hemlock Bark	20	93.3	10.98	78
		46.7	10.60	72
		26.7	9.76	58
		13.3	9.35	52
		6.7	7.98	29
Oak Bark	4.11	93.3	25.02	94
		46.7	24.59	91
		23.3	24.01	86
		11.7	22.09	72
		5.9	18.77	46
Larch Bark	4.37	93.3	28.10	140
		46.7	24.52	109
		23.3	21.97	88
		11.7	19.10	63
		5.9	16.24	39
Chestnut Wood	15	93.3	26.87	126
		46.7	25.80	117
		26.7	24.59	107
		23.3	23.52	98
		16.0	22.49	89
Sumac	4	93.3	24.98	160
		46.7	25.05	161
		23.3	24.47	155
		11.7	23.45	144
		5.9	21.45	123
Osage Orange	8	93.3	40.48	203
		46.7	39.47	195
		26.7	38.21	186
		13.3	36.27	171
		9.3	35.67	167
Gambier	4.58	93.3	29.04	273
		46.7	25.60	229
		23.3	22.56	190
		11.7	17.22	121
		5.9	13.38	72

are nothing short of sensational, they are probably not at all exaggerated. But the extent of these errors is less surprising in view of the large proportion of such nontannins as gallic acid that appear as tannin by the A.L.C.A. method, as shown in Tables XVII and XVIII.

The need for arbitrary limits in the A.L.C.A. method was clearly shown by the gallic acid experiments, but was more strongly emphasized by similar experiments upon actual tan liquors. The effect of altering the proportion of hide powder with solutions of the 8 tanning materials is shown in Table XXI and in Figs. 88, 89, and 90. In Figs. 88 and 89 the short, vertical lines are placed at points on the curves corresponding to the smallest amount of hide powder that would completely detannize the solutions under the conditions of the A.L.C.A. method, as determined by the gelatin-salt test. The crosses indicate the points corresponding to the quantity of hide powder called for in the A.L.C.A. method. The zero points represent the percentages of tannin found by the Wilson-Kern method and the broken portions of the curves are extrapolated.

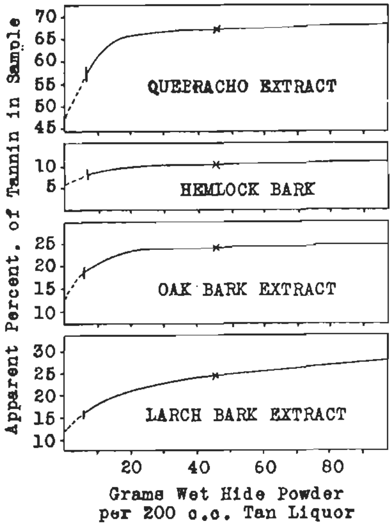


FIG. 88. — Effect of variation in amount of hide powder used upon the determination of tannin by A.L.C.A. method.

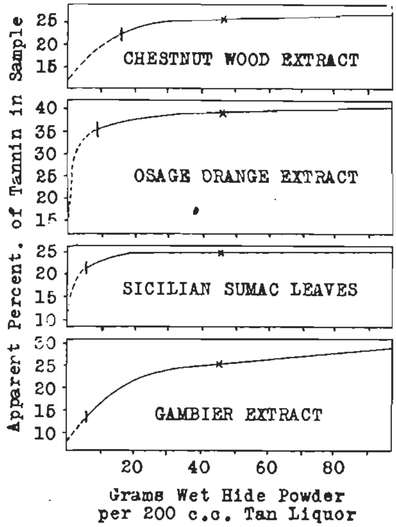


FIG. 89. — Effect of variation in amount of hide powder used upon the determination of tannin by A. L. C. A. method.

No scientific reason has ever been given for the selection of the particular amount of hide powder called for in the A.L.C.A. method. So far as the principle of the method is concerned, any of the values given in Table XXI might be accepted as correct, since the solutions were completely detannized in every case. This should be borne in

mind when employing figures for tannin appearing in the literature, which have been found by this or similar methods.

As would be expected, the greatest errors in the A.L.C.A. method are obtained with those materials containing the greatest proportion of nontannin to tannin. Quebracho, having least nontannin, gives the smallest error. However, if the quebracho is mixed with gallic acid to make the proportion of nontannin to tannin about the same as in the case of the gambier, it gives errors nearly as great as in the case of the gambier, which is shown in Table XXII.

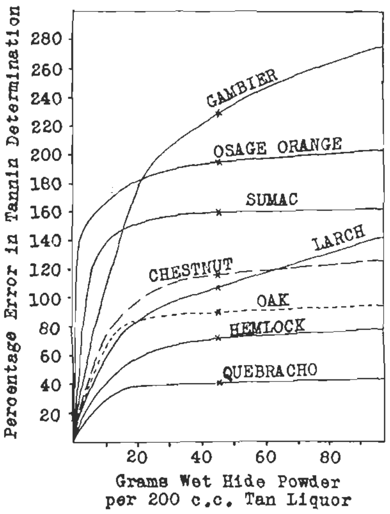


FIG. 90.—Effect of variation in amount of hide powder used upon the error involved in determining tannin by the A.L.C.A. method.

Comparison of the two methods has brought out at least one fact of practical significance: Those materials which give the least errors by the A.L.C.A. method are most astringent, while those giving greatest errors are least astringent. The order of the materials in Table XX might almost be taken as the order of decreasing stringency, although an exact parallelism cannot be claimed. Quebracho and hemlock bark are generally conceded to be the most astringent and sumac and gambier the least astringent of these materials. This suggested a relation

TABLE XXII.

MIXTURE OF QUEBRACHO EXTRACT AND GALLIC ACID.

Wet Hide Powder (73 per cent water) Used to Detannize 200 cc. Tan Liquor Grams	Percentage Analysis of Mixture of 5 Parts of Quebracho Extract to 9 Parts of Dry Gallic Acid					Percentage Error in A. L. C. A. Method		
	Water	A. L. C. A. Method Insoluble Matter	Soluble Matter Nontannin	Tannin	Wilson-Kern Method Tannin	Alone (from Fig. 90)	In Presence of Gallic Acid	Gambier Alone
93.3	5.80	3.96	33.87	56.37	16.93	44	233	273
46.7	5.80	3.96	37.14	53.10	16.93	43	214	229
23.3	5 80	3.96	44.07	46.17	16.93	39	173	190
11.7	5.80	3.96	53.39	36.85	16.93	33	118	121
5.9	5.80	3.96	63.34	26.90	16.93	18	59	72

between astringency and the ratio of nontannin to tannin. Astringency appears to be a function of the rate of combination of tannin and protein. In the experiments listed in Table XIX, the hide powder

fixed more than twice as much tannin from the quebracho liquors in 3 hours as from the gambier liquors in 6 hours. But, when enough gallic acid was added to the stronger quebracho liquors to give them the same ratio of nontannin to tannin as in the gambier, the hide powder did not remove anywhere nearly all the tannin in 6 hours. Upon addition of the gelatin-salt reagent to the liquors after the 6-hour shaking, huge precipitates were formed, suggesting a great reduction in astringency. That the effect was only one of slowing up the tanning action was proved by the fact that the hide powder was able to detannize the solution completely in 24 hours. This also explains the mild action of tan liquors which have been used a great many times and have consequently accumulated a large amount of nontannin.

The polemics following the publication of the Wilson-Kern method served to stimulate investigations of the properties of tanning materials. At the 17th annual meeting of the American Leather Chemists Association a formal discussion [20] of the Wilson-Kern method was staged, and the chief aim of the opposition was apparently to show that the low results obtained were due to losses of tannin in the manipulation. It was contended that a certain proportion of the tannin of a liquor will form a stable compound with hide only after long contact, and, further, that even tannin which has already combined with the hide powder will be removed to an appreciable extent during the washing required by the Wilson-Kern method, but no substantial evidence was offered in support of these contentions.

Effect of Washing.

Certain differences in behavior of the several different tanning materials have caused a widespread belief that some tannins form more stable compounds with skin that others; for example, the tannin from gambier is supposed to form a compound with skin less stable than that from hemlock bark. It has also been supposed that mixtures of tanning materials behave differently in this respect from the individual materials.

Wilson and Kern [21] made a careful study of the possible losses of tannin during the washing operation involved in their method and came to the conclusion that any such loss was too small to have any effect upon the determination. Table XXIII shows that practically the same results are obtained for a great variety of tanning materials, whether the tanned hide powders were washed 15, 25, or 50 times. Theoretically, tanning may be reversible, but the rate of hydrolysis is so small as to have no bearing on the Wilson-Kern method, which holds equally well for both mild and astringent tanning materials.

[20] Printed in full, *J. Am. Leather Chem. Assoc.* 15 (1920), 451.
[21] Nature of the Hide-Tannin Compound and Its Bearing upon Tannin Analysis. J. A. Wilson and E. J. Kern. *J. Ind. Eng. Chem.* 12 (1920), 1149.

TABLE XXIII.

EFFECT OF EXCESSIVE WASHING OF THE TANNED HIDE POWDER UPON THE PER CENT OF TANNIN FOUND BY THE WILSON-KERN METHOD.

Extract	Extract Grams in 200 cc. Solution	Hide Substance in Powder Used to Detannize 200 cc. Solution Grams	Per cent Tannin in Extract. Value Obtained from Analysis of Tanned Powder Washed 15 Times	25 Times	50 Times
Quebracho	3.80	10.44	46.84	47.25	46.90
Gambier	10.00	10.44	7.87	7.89	7.67
Gambier-quebracho mixture *	6.90	10.44	20.67	20.34	20.43
Chestnut wood	13.60	10.32	... ‡	13.99	13.93
Hemlock bark	13.00	10.32	23.47	23.38	23.50
Chestnut wood - hemlock bark mixture †	13.30	10.32	... ‡	18.73	19.05
Oak bark	13.60	10.40	15.52	15.36	15.35
Larch bark	13.60	10.32	—. ‡	11.29	11.28
Sumac	13.00	10.39	16.36	16.29	16.39
Wattle bark	8.00	10.32	24.66	24.16	24.73

* Mixture of 10 parts solid quebracho extract to 50 of gambier extract.
† Mixture of 68 parts of chestnut wood extract to 65 of hemlock bark extract.
‡ Calculation not made because 15th wash water gave test for nontannin with ferric chloride.

Conversion of Nontannin into Tannin.

In criticizing the Wilson-Kern method, Schultz [22] said, "We have taken the nontannins and washings and reconcentrated them under a high vacuum to the original volume of 200 cc. and have tanned hide powder with it, and, by the calculations employed, we have found a definite percentage of tannin." He mentioned also that the concentrated liquor gave a positive test for tannin with the gelatin-salt reagent. It might look at first sight as though the detannized liquor and wash waters, before concentrating, really had contained tannin and Schultz evidently so regarded it. Wilson and Kern confirmed Schultz's experimental finding while analyzing a sample of gambier extract by their new method. The detannized liquor and 15 wash waters, all of which gave no test with the gelatin-salt reagent, were concentrated to 200 cubic centimeters, whereupon they were found to give a bulky precipitate with the reagent. But, when diluted back to 3200 cubic centimeters, they still gave a bulky precipitate with the gelatin-salt reagent, showing that a most important chemical change had taken place during the concentrating.

Another sample of gambier was analyzed by the new method and found to contain 7.94 per cent of tannin. The detannized liquor and 17 wash waters, 3600 cubic centimeters in all, were evaporated to 250 cubic centimeters, analyzed by the new method, and found to contain

[22] (Discussion), *J. Am. Leather Chem. Assoc.* 15 (1920), 455.

5.56 parts of tannin per 100 of original extract, giving the extract a total of 13.50 per cent tannin. The detailed results are given in Table XXIV.

TABLE XXIV.

Gambier Extract.

Two hundred cubic centimeters of solution containing 9.00 grams of extract were detannized with 12 grams of air-dry hide powder, containing 10.40 grams of hide substance, and then the tanned powder was washed 17 times with a total of 3400 cubic centimeters of water. The residual liquor and wash waters were evaporated to 250 cubic centimeters and used to tan 12 grams of fresh hide powder, which was afterwards washed as usual.

	Hide Powder Tanned in	
Analysis of Air-Dry, Tanned Powder	Original Solution	Concentrated Wash Waters
Water	17.31	16.24
Ash	0.16	0.14
Fat (chloroform extract)	0.39	0.42
Hide substance (N x 5.62)	76.86	79.38
Tannin (by difference)	5.28	3.82
Per 100 grams hide substance:		
Tannin found, grams	6.87	4.81
Material used, grams	86.54	86.54
Per cent tannin in extract	7.94	5.56

Total tannin, either originally present or formed during the concentrating of the wash waters, 13.50 per cent.

In order to show that this increased amount of tannin would have combined with the hide powder had it been present in the original solution, Wilson and Kern made up a new solution of this extract, concentrated and diluted back several times, and then analyzed it by the new method, finding 12.69 per cent tannin. If the concentrating had been continued a little longer, the figure 13.50 would probably have been reached or passed. The results are shown in Table XXV.

TABLE XXV.

Gambier Extract.
(Same as noted in Table XXIV.)

Dissolved 60.00 grams of extract in 1 liter of water. Concentrated to 250 cubic centimeters and diluted back to 1 liter. Repeated 3 times, the fourth time diluting to 2 liters. Two hundred cubic centimeters of diluted solution, containing 6.00 grams of original extract, were detannized with 12 grams of air-dry hide powder containing 10.37 grams of hide substance, which was afterwards washed as usual.

ANALYSIS OF AIR-DRY TANNED POWDER.

Water	18.23
Ash	0.18
Fat (chloroform extract)	0.42
Hide substance (N x 5.62)	75.62
Tannin (by difference)	5.55
Per 100 grams hide substance:	
Tannin found, grams	7.34
Material used, grams	57.86
Per cent tannin in extract	12.69

In spite of the great change in the tan liquor produced by concentrating, it is not shown to any appreciable extent in the analyses by the A.L.C.A. method shown in Table XXVI. Concentrating the tan liquor and diluting back caused a rise in per cent of tannin by the new method from 7.94 to 12.69, but the rise in the A.L.C.A. method is only from 26.14 to 26.40, which difference is so small as even to be attributable to experimental error. The reason for this small difference is probably that the nontannins which are convertible into tannin all combine with the hide powder initially, even though they are easily removed later by washing.

TABLE XXVI.

GAMBIER EXTRACT.
(Same as noted in Table XXIV.)

Both the original liquor noted in Table XXIV and the specially treated liquor noted in Table XXV were appropriately diluted and analyzed by the A. L. C. A. method.

	Per Cent of Original Extract	
	Original Liquor	Treated Liquor
Insoluble matter	7.66	8.62
Nontannin	18.33	17.57
Tannin	26.14	26.40

Just what chemical actions are involved in the conversion of nontannin to tannin must remain a matter for speculation until more data are available; oxidation, condensation, and polymerization may all be involved. It is conceivable that gallic acid might be converted into digallic acid under suitable conditions, and it seems extremely likely that a polymerized form of digallic acid would have tanning properties. A solution of pure gallic acid gives no test for tannin, but Wilson and Kern found that after boiling for some time it gives a bulky precipitate with the gelatin-salt reagent, and will then apparently tan skin. A detannized solution, which gives no test for tannin, can be made to give a strong test merely by passing oxygen gas through it. Long exposure to air has a similar action. It is evident that the Wilson-Kern method furnishes a valuable means of studying the conversion of nontannin into tannin, and might conceivably be applied to a study of the formation of tannin in nature and to the aging of barks.

Effect of Aging.

The conversion of nontannin into tannin is apparently responsible for two factors of great importance to tanners of heavy leathers, namely, the time factor in tanning and the aging of leather. In the A.L.C.A. discussion referred to, Alsop[23] remarked that sole leather tanned slowly not only contains more tannin, but actually consumes

[23] *Loc. cit.*, p. 464.

less tanning material than the rapid tannages. In a private communication to the author, H. R. Procter has called attention to the fact that leather stored for a long time, or aged, before washing contains more tannin than if it had been washed immediately after tanning. A number of critics have said that the Wilson-Kern method is weak because it does not include as tannin all of the material that can be made to combine with hide substance by aging. This argument, however, is weak because the Wilson-Kern method offers a very satisfactory means of studying the aging properties of different tanning materials. An application of the method to such a study is shown in Table XXVII for ten commercial extracts or mixtures thereof.

TABLE XXVII.

Effect of Aging upon Per Cent of Combined Tannin in Leather.

Three 12-gram portions of hide powder were used to detannize 200 cubic centimeters each of the solutions of tanning materials noted in Table XXIII. One portion in each case was washed 25 times immediately after tanning and the other two were allowed to dry without washing. Of these one was kept exactly 30 days and then washed 25 times; the other was kept just 1 year and then washed 25 times.

	Tannin as Per Cent of Original Extract By Wilson-Kern Method			
Extract	In Leather Washed Immediately after Tanning	In Leather Kept 30 Days before Washing	In Leather Kept 1 Year before Washing	By A. L. C. A. Method
Quebracho	47.25	53.00	54.59	60.87
Gambier	7.89	10.49	13.13	25.61
Gambier-quebracho mixture	20.34	23.92	25.34	33.22
Chestnut wood	13.99	18.02	18.36	25.70
Hemlock bark	23.38	24.87	25.46	26.68
Chestnut wood-hemlock bark mixture	18.73	20.45	21.25	25.64
Oak bark	15.36	17.23	20.08	26.19
Larch bark	11.29	13.22	18.73	22.96
Sumac	16.29	17.94	17.96	25.51
Wattle bark	24.16	25.89	26.61	33.55

It is interesting to note that in no case does aging for an entire year raise the tannin value to a point as high as that given by the A.L.C.A. method. Aging the gambier-tanned powder for a year raised the tannin content to about the same value as is produced by merely concentrating the liquor before tanning, as indicated in Tables XXIV and XXV. The change taking place upon aging is probably of the same nature as that described above as the conversion of nontannin into tannin.

In the manufacture of vegetable-tanned upper leather, the effect of aging is probably not very marked. In actual practice, Wilson and Kern found barely 50 per cent as much tannin in the leather coming from a certain upper leather yard during a 3-year period as was put into it, according to the analyses by the A.L.C.A. method of the

extracts used. About half of the tannin seemed to be mysteriously disappearing until they applied their new method to the control of the yard and found that the amounts of tannin used and those found in the finished leather then checked easily within the limits of experimental error.

In the manufacture of sole leather, one would expect the effects of aging to be much more pronounced. It seems reasonable to suppose that the Wilson-Kern method could be applied to a sole leather yard by keeping the tanned powders in the dried state for a sufficient length of time before washing to correspond to the conditions under which the sole leather was kept. That the A.L.C.A. method is no more reliable for heavy leather work than for upper leather is indicated by the following figures which have been made available to the author: Of 100 lbs. of tannin, as determined by the A.L.C.A. method, that enter the leach house, only 39 lbs. appear as combined tannin in the finished leather. Losses in the spent tanning material, waste liquors, and water soluble matter from the leather were determined only by the A.L.C.A. method, but even with all this taken into consideration, there remains a large loss that can be accounted for only on the assumption that the A.L.C.A. method gives results much too high.

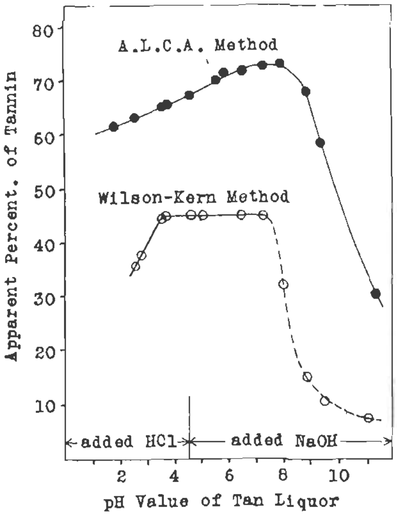


FIG. 91.—Effect of pH value upon the determination of tannin in a sample of quebracho extract.

Effect of pH Value.

Thompson, Seshachalam, and Hassan[24] made a preliminary study of the effect of adding acetic and hydrochloric acids to extracts of quebracho, mimosa, mangrove, gambier, myrobalans, chestnut wood, and oak wood and found that the addition of small amounts of acid affected practically all of the determinations made. Fig. 91, taken from a paper by Wilson and Kern,[25] shows how the determination of tannin, by both the A.L.C.A. and the Wilson-Kern methods, is affected by change of pH value. The latter method gives a practically constant value over the wide range 3.6 to 7.3. Where the falling off in per cent of tannin occurs at pH values higher than 7, indicated by the broken line, the results should not be considered as found by this method because in each case the residual solution gave a test for tannin, by the gelatin-salt test, whereas the method specifies that the determination is to be discarded whenever such a test is

[24] Influence of Degree of Acidity on the Tannin Content of Solutions. F. C. Thompson, K. Seshachalam, and K. Hassan. *J. Soc. Leather Trades Chem.* 5 (1921), 389.
[25] Effect of Hydrogen-Ion Concentration upon the Analysis of Vegetable Tanning Materials. J. A. Wilson and E. J. Kern. *J. Ind. Eng. Chem.* 14 (1922), 1128.

obtained. The values obtained were included in the curve in order to show the effect of pH value on the rate of tanning.

Modified Wilson-Kern Method.

In order to meet the demand for a simpler method, Wilson and Kern[26] modified their method as follows: Standard hide powder is further purified by washing with water to free it from soluble matter, then dehydrating with alcohol, then soaking in two changes of xylene, and then drying. The tan liquor is filtered, as in the A.L.C.A. method, and only the soluble portion used, 100 cubic centimeters being shaken with 2 grams of purified hide powder for 6 hours. The tanned powder is allowed to wash over night in a specially designed percolator and is then dried and weighed. The increase in weight of the dry powder represents the weight of tannin in the 100 cubic centimeters of solution used. Wilson and Kern compared the modified and original procedures of their method and found that they give practically identical results for all ordinary extracts. For further details, the original papers should be consulted.

Potential Difference of Tannin Solutions.

In Chapter 5 it was pointed out that the stability of a colloidal dispersion is determined less by the absolute value of the electrical charge on the particles than by the electrical difference of potential between the film of solution wetting the particles and the bulk of the surrounding solution. In the Procter-Wilson theory of tanning, to be discussed in Chapter 13, the astringency of a tan liquor in practice is assumed to be a function of the potential difference between the solution immediately in contact with the tannin particles and the bulk of the tan liquor as well as of the potential difference between the tan liquor and the collagen jelly. Grasser[27] studied the electrochemistry of tannin solutions, but obtained confusing results of rather doubtful value, which may be due to his failure to control or measure the hydrogen-ion concentrations of the liquors.

Thomas and Foster[28] were more successful. Using the U-tube electrophoresis method described by Burton,[29] they succeeded in measuring the potential differences of tannin solutions under different conditions. Table XXVIII shows a series of values obtained for tan liquors made from 8 typical tanning materials. It is interesting to find gambier, the mildest tanning material, with the lowest potential difference and quebracho, the most astringent, with the highest potential difference. The order of decreasing conductivity of these solutions

[26] The Determination of Tannin. J. A. Wilson and E. J. Kern. *J. Ind. Eng. Chem.* 13 (1921), 772.

[27] Electrochemistry of Tannins. G. Grasser. *Collegium* (1920), 17, 49, 277, 332.

[28] The Colloid Content of Vegetable Tanning Extracts. A. W. Thomas and S. B. Foster. *J. Ind. Eng. Chem.* 14 (1922), 191.

[29] Physical Properties of Colloidal Solutions. E. F. Burton. Longmans, Green & Co., London (1916).

was sumac, gambier, oak bark, larch bark, hemlock bark, chestnut wood, osage orange, quebracho. It is evident that the potential difference is not a simple function of the conductivity, but is influenced by the kind as well as the amount of electrolyte present.

TABLE XXVIII.

POTENTIAL DIFFERENCES OF TANNINS FROM DIFFERENT SOURCES.

Extract	Grams Total Soluble Matter per liter	Potential Difference volts
Gambier (cube)	18.7	—0.005
Oak bark	17.0	—0.009
Chestnut wood	17.8	—0.009
Hemlock bark	16.7	—0.010
Sumac	19.6	—0.014
Larch bark	19.5	—0.018
Osage orange	13.7	—0.018 (?)
Quebracho	11.0	—0.028

If the absolute value of the electrical charge on the particles remains constant, according to the theory given in Chapter 5, the potential difference at the surface should decrease with increasing concentration of electrolyte, or increase with decreasing concentration. Thomas and Foster found that the potential difference of solutions of quebracho extract actually does increase with decreasing concentration, as shown in Table XXIX. The addition of acid decreases the value of the potential difference by lowering the absolute value of the electrical charge, which holds true for negatively charged dispersions in general. This is shown in Table XXX.

TABLE XXIX.

POTENTIAL DIFFERENCES OF SOLUTIONS OF QUEBRACHO EXTRACT.

Concentration Grams Dry Solids per liter	Potential Difference volts
32	—0.024
16	—0.028
8	—0.029
4	—0.030

TABLE XXX.

EFFECT OF ADDITION OF ACID.

(16 grams of solid quebracho extract per liter.)

0.1 *N* HCl added per liter cubic centimeters	Potential Difference volts
0	—0.024
10	—0.014
15	—0.010
20	approx. 0

The effect of dialyzing a tan liquor is to lower the concentration of electrolyte, which we should expect to increase the potential dif-

ference. The values in Table XXXI show that this actually occurs, although part of the increase may be attributed to dilution.

TABLE XXXI.

EFFECT OF DIALYSIS.

Extract	Grams Extract in 250 cc.	Hours Dialyzed	Final Volume cc.	Potential Difference volts
Quebracho	4	60	415	— 0.033
Osage orange	4	24	370	— 0.024
Sumac	4	24	460	— 0.026
Gambier	8.2	24	390	— 0.029
Hemlock bark	...	24	...	— 0.024

Isoelectric Points of the Tannins.

Thomas and Foster [30] later extended their investigations in an attempt to determine the isoelectric points of tannins from different sources. The various tanning extracts were dissolved in a citrate buffer mixture having a pH value of 2.0 and the solutions were finally adjusted to the desired pH values by means of the hydrogen electrode. The buffer was apparently necessary to eliminate, or delay, the secondary actions, such as diffusion of the boundaries and change of reaction of the extracts due to electrolysis, which behavior had nullified previous experiments.

Between the pH values 2.5 and 2.0, the direction of migration of the tannin particles changed from anodic to cathodic in solutions of the extracts of oak bark, hemlock bark, wattle bark, sumac, and gambier. In the case of quebracho, there seemed to be no movement in the U-tube at the pH values 3.0 or 2.5, but at 2.0 the movement seemed to be slightly cathodic. Quebracho was precipitated by the buffer and only the clear, supernatant liquor could be used, which may account for the inability to obtain more definite results.

Until they are located more definitely, the isoelectric points of the tannins may be accepted as lying between the pH values 2.0 and 2.5, at least those of hemlock, oak, and wattle barks, sumac, and gambier.

Precipitation of Tan Liquors.

In the hope of throwing some light upon the colloidal nature of the tannins, Thomas and Foster studied the action of various electrolytes upon a great variety of tan liquors. Aqueous solutions of different tanning extracts were made up so that 100 cubic centimeters of solution contained 4 grams of solid matter. The solutions were made at 85° C., cooled to 25°, and then adjusted to final volume. The stock solution was then centrifuged for 5 minutes at 1000 times gravity in

[30] The Electrical Charge of Vegetable Tannin Particles. A. W. Thomas and S. B. Foster. *Ind. Eng. Chem.* (1923); (advance copy).

order to throw down coarse suspended matter. Portions of 25 cubic centimeters were put into 100-cubic centimeter, graduated oil tubes. Then 25 cubic centimeters of the electrolyte were added, the solutions were allowed to stand for 15 to 30 minutes for precipitation to start, and were then centrifuged for 5 minutes at 1000 times gravity. The volumes of the precipitates were recorded and plotted against the concentrations of electrolyte employed.

The results may be most conveniently studied by grouping them under the names of the various electrolytes used. Each available extract was not tested with all electrolytes because, in some cases, preliminary experiments indicated that further work would be fruitless.

Monovalent Cations.

Potassium chloride. Concentrations of potassium chloride from 0.02 to 4 molar gave only negligible amounts of precipitate with gambier and quebracho. Oak bark gave a gradually increasing salting out effect.

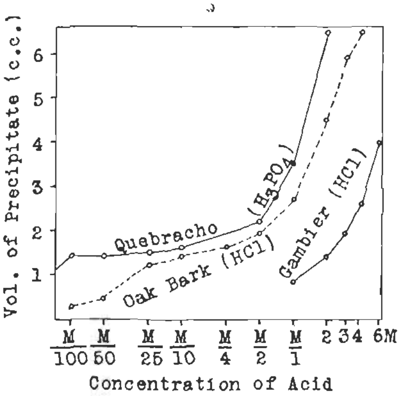


Fig. 92.—Precipitation of Tannins by Hydrochloric and Phosphoric Acids.

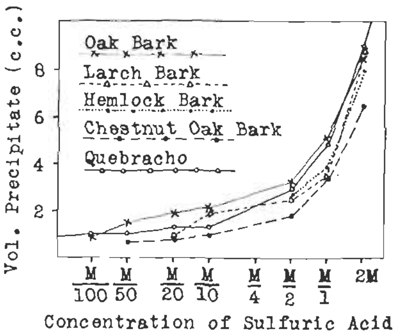


Fig. 93.—Precipitation of Tannins by Sulfuric Acid.

Since gambier and quebracho represent extreme types of tanning extracts, no further tests were made with this salt. It must be borne in mind that the solutions to which the neutral salts were added were made simply by dissolving the extracts in distilled water and had pH values in the vicinity of 4.5.

Hydrochloric acid. Concentrations from 0.01 to 6 molar were used. Gambier and quebracho gave large amounts of precipitate only at high concentrations of acid and, since this was not a simple colloid precipitation, no further experiments were attempted. A salting out effect was obtained with oak bark. (See Fig. 92.)

Sulfuric acid. Quebracho, hemlock bark, oak bark, and larch bark gave progressively increasing amounts of precipitate with increasing concentration of acid, as shown in Fig. 93. No precipitate was obtained with sumac until molar concentration was reached, when gummy

masses were thrown down, similar to those obtained with aluminum sulfate. At 4 molar concentration, a flocculent precipitate was formed.

Phosphoric acid. Gambier began to give an appreciable precipitate only at 4 to 7 molar concentration. With sumac a gummy mass was thrown out at 2 molar, as was observed upon the addition of sulfuric acid and aluminum sulfate, and at 4 to 7 molar a flocculent precipitate formed which left the supernatant solution almost colorless. Quebracho was progressively salted out. (See Fig. 92.)

Acetic acid. Experiments with quebracho, sumac, gambier, and oak bark were run with concentrations of acid from 0.005 to 4 molar. There was no appreciable precipitation in any case. At the higher concentrations the suspended matter began to dissolve.

Formic acid. Concentrations from 0.005 to 12.5 molar were used. Sumac, chestnut oak bark, larch bark, gambier, and hemlock bark

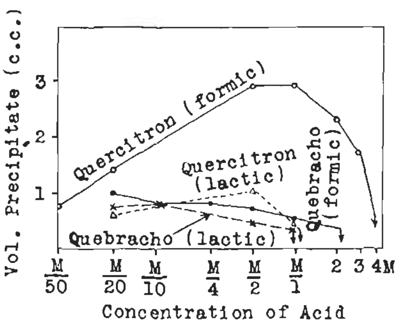


FIG. 94.—Precipitation of Tannins by Formic and Lactic Acids.

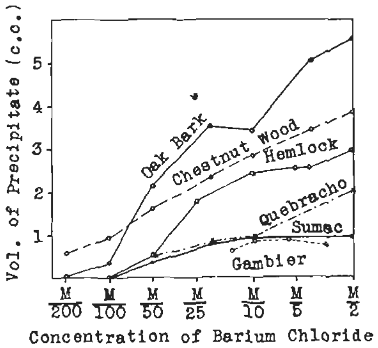


FIG. 95.—Precipitation of Tannins by Barium Chloride.

gave no precipitation up to 4 molar, at which concentration the suspended matter began to dissolve. Quebracho and quercitron bark were precipitated, but the precipitate redissolved at from 2 to 4 molar. (See Fig. 94.)

Lactic acid. Concentrations from 0.005 to 2 molar were employed. The effects of this acid were similar in kind, but not in degree, to those with formic acid. (See Fig. 94.) The precipitates with quebracho and quercitron redissolved at lower concentrations of lactic than of formic acid. Since lactic is the weaker acid and since this redissolving was not found with hydrochloric or sulfuric acids, the effect must be due to chemical properties other than those of the hydrogen ion. This is an important point to consider in the chemical control of tan liquors.

Divalent Cations.

Barium chloride. On account of the limit of solubility, this salt was employed up to only 0.5 molar. The salting out effect is shown in Fig. 95.

Calcium chloride. Concentrations up to 2 molar were used. As with barium chloride, increasing amounts of precipitate were obtained with the different tanning materials used, as shown in Fig. 96. At the same concentration of these salts the different extracts gave in some

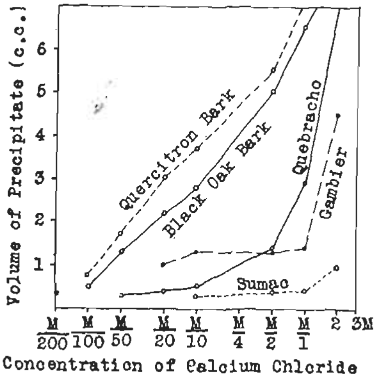


FIG. 96.—Precipitation of Tannins by Calcium Chloride.

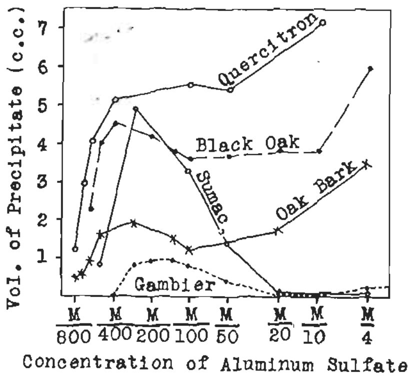


FIG. 97.—Precipitation of Tannins by Aluminum Sulfate.

cases less, and in others more, precipitate, showing the presence of substances reacting with barium and calcium ions to form compounds of different solubilities.

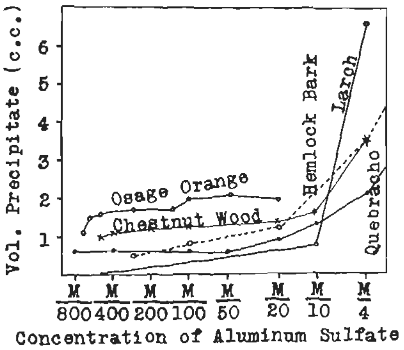


FIG. 98.—Precipitation of Tannins by Aluminum Sulfate.

Trivalent Cation.

Aluminum sulfate. In the precipitation of negatively charged colloidal dispersions, aluminum sulfate is not only a powerful precipitant, but it also gives the "irregular series" or "tolerance zone" which is typical of the action of weak base cation-strong acid anion salts, as shown by Buxton and Teague,[31] and by Freundlich and Schucht.[32] The concentrations of aluminum sulfate used ranged from 0.00125 to 0.5 molar.

The "irregular series" effect was obtained with gambier, sumac, oak bark, and quercitron bark. Precipitation generally set in at 0.00125 molar concentration, rose rapidly to a maximum, dropped off into a "tolerance zone," and then started upward again, as shown in Fig. 97.

Those which gave no "irregular series," at least up to 0.5 molar concentration of the salt, were osage orange, quebracho, camel cutch, chestnut wood, chestnut oak bark, hemlock bark, and larch bark, shown

[31] *Z. physik. Chem.* 57 (1907), 76.
[32] *Ibid.*, 85 (1913), 641.

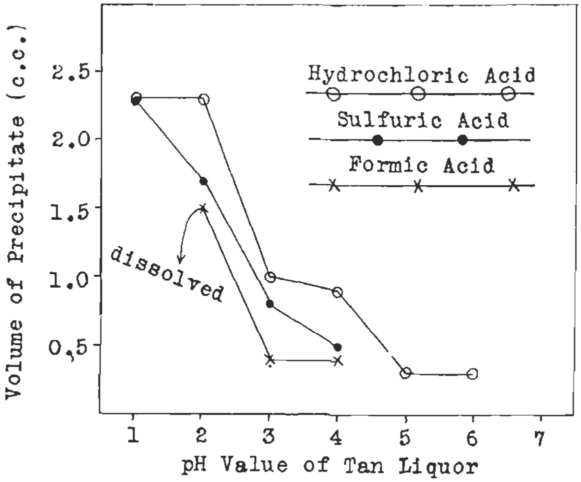


FIG. 99.—Precipitation of Tannins of Quebracho Extract as a Function of pH Value.

in Fig. 98. Precipitation started at 0.00125 molar and increased gradually to about 0.1 molar, where there was an abrupt upward trend similar to a salting out effect. These extracts are not so sensitive to precipitation by dilute solutions of aluminum sulfate as those shown

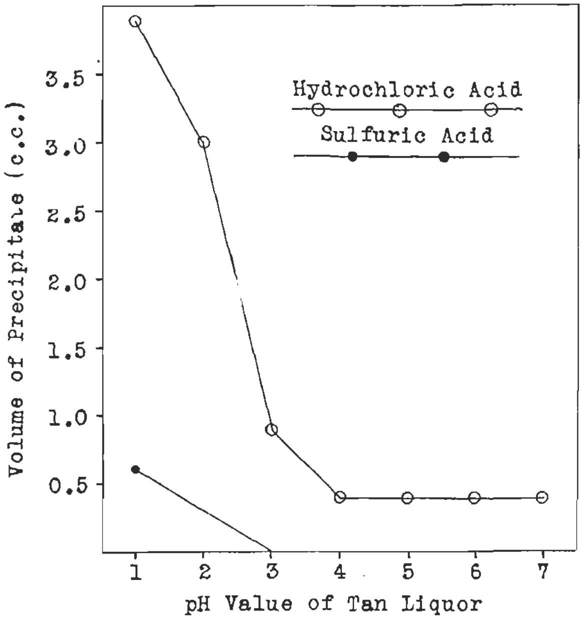


FIG. 100.—Precipitation of Tannins of Gambier Extract as a Function of pH Value.

in Fig. 97. Bengal cutch seemed to be in a separate category, since it was unaffected by the addition of aluminum sulfate.

Hydrogen-Ion Concentration.

The effect of hydrogen-ion concentration upon the precipitation of solutions of quebracho, gambier, larch bark, and oak bark by sulfuric, hydrochloric, and formic acids is shown in Figs. 99, 100, 101, and 102. Solutions of sumac, hemlock bark, and wattle bark were not precipitated by these acids with increasing acidity to pH = 1. It is evident that the volume of precipitate formed is not a function of

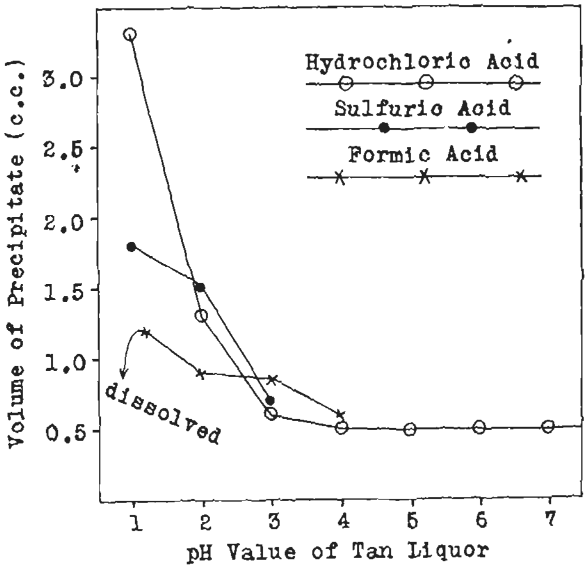


FIG. 101.—Precipitation of Tannins of Larch Bark Extract as a Function of pH Value.

hydrogen-ion concentration alone, since the three acids give curves of different shapes.

Wherever a precipitate formed, the amount invariably increased with increasing hydrogen-ion concentration where hydrochloric and sulfuric acids were used. But an increasing concentration of formic acid dissolved the precipitate, or the suspended matter in cases where no precipitate had previously formed.

The precipitates obtained with hydrochloric acid were found to be soluble in strong alcohol and in 9 molar lactic acid. On shaking up with water, these precipitates dispersed, but gradually settled out more or less completely in 24 hours. In the case of oak bark and quebracho, it was found that approximately two-thirds of the original solid matter present had been precipitated at pH = 1.

When the pH value was increased by the addition of sodium hydroxide, there was increasing solution, clear liquids being obtained in every case at pH = 8. The effect of adding calcium hydroxide, however, is very different, as will be recalled from Fig. 87 of Chapter 11.

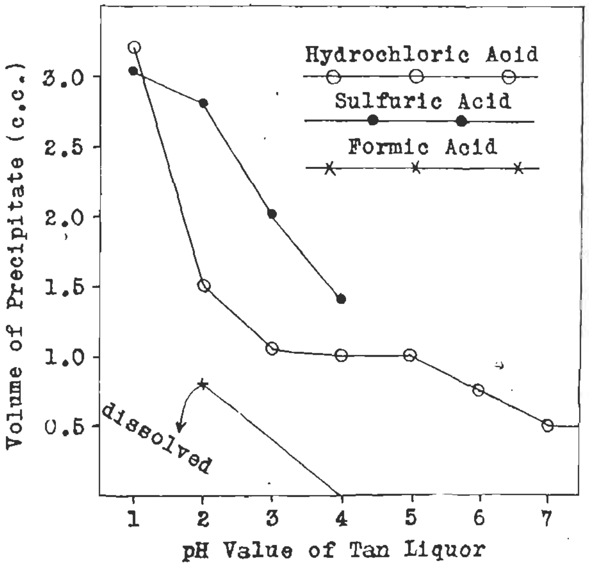


FIG. 102.—Precipitation of Tannins of Oak Bark Extract as a Function of pH Value.

At pH values above 7.2 increasing amounts of precipitate are obtained with increasing pH value.

The conduct of the extracts examined by Thomas and Foster shows that they contain a large amount of colloidal matter of a type of dispersion with properties between those of the intermediate and hydrophilic dispersions. From the colloidal point of view, vegetable tanning materials furnish an almost unexplored field; the work outlined in this chapter cannot be considered as more than a good start.

Chapter 13.

Vegetable Tanning.

Raw skin is readily putrescible in the wet state. Upon drying, the collagen fibers become glued together and the skin becomes very stiff. Although the dried skin will not putrefy, it again becomes putrescible as soon as it comes into contact with water. Thousands of years ago the discovery was made that the properties of skin substance change completely when the wet skin is brought into contact with the aqueous extract of those forms of plant life which have since come to be classed as vegetable tanning materials. The action which brings about this change of properties is known as vegetable tanning and the compound of skin protein and tannin as leather. Under normal conditions, the fibers of leather do not glue together upon drying and they are not putrescible even in the wet state.

The practice of tanning is greatly complicated by the necessity for endowing the leather with many delicate properties, according to the use to which it is to be put, all of which are markedly affected by slight differences in manipulation. The effect produced by any single change in the tanning process depends upon the nature of every one of the numerous operations preceding and following that in which the change has been made. In the manufacture of one type of leather, a skin may be subjected to scores of different operations and a slight change in any one of these may necessitate changes in nearly all of the others in order to preserve the specific properties desired in the finished leather. It is this fact that renders most practical treatises of leather manufacture of so little value to the tanner. Were he to try to adopt an operation described in the literature which was better in itself than the one he was using, he might find that the change would spoil his leather because of its failure to harmonize with all of the other operations peculiar to his particular process. There are, however, certain broad principles of tanning which are followed generally.

Two conditions may be accepted as essential to successful tanning: the first that the natural physical structure of the skin shall be changed but very little; the second that the degree of tannage shall be as nearly uniform as possible throughout the skin. The second condition, in a large measure, is essential to the first.

The physical means widely adopted to preserve the natural structure of the skins during tanning is to suspend them freely from sticks with the heads hanging downward in the tan liquors, care being taken to see that the unhaired skin is free from creases or wrinkles, which

would be permanently fixed by the tannage. Usually the lower end of each skin is tacked onto a stick and the skin is then spread out carefully so that it hangs in its natural condition when immersed in the tan liquor. The supporting stick rests upon a rectangular frame floating in the liquor. The skins are not subjected to any violent mechanical agitation until the grain surface has been "set" by the tannage and the tannins have penetrated into the skin for a considerable distance.

If skins from the beamhouse were put directly into strong tan liquors of such reaction that the rate of combination of tannin with the skin protein was abnormally great compared to the rate of diffusion of tannin into the interior of the skin, the tendency for the outer layers to assume an area different from that of the skin as a whole would cause a distortion of the skin that would be permanent. In such a case, the liquor is called very astringent. The fact is often overlooked that the reaction of the solution previously absorbed by the skin may be as important in bringing about this condition as the reaction of the tan liquor itself. In fact a given tan liquor may appear very astringent to a pickled skin and yet very mild to a skin taken directly from the bate liquor. The distortion may show itself as coarse wrinkles, as the finer reticulation illustrated in Fig. 48 of Chapter 5, or merely as a rough grain surface. Since these distortions greatly lower the value of the leather, every effort is made to avoid them.

The practical means adopted by the tanners to eliminate this danger is to hang the skins from the beamhouse first in a tan liquor which has been used to tan a great many lots of skins previously and in which the ratio of nontannin to tannin is very great. Each day the skins are then moved into stronger and fresher liquors until completely tanned. The effect of an increasing ratio of nontannin to tannin in the tan liquor is to increase the ratio of the rate of diffusion of the tannin into the skin to the rate of combination of the tannin with the skin protein. This has the obvious effect of making the rate of combination more uniform throughout the skin, and consequently lessening the tendency towards distortion. The ideal process would be the one in which combination was entirely prevented until the tannin was uniformly distributed throughout the skin and then allowed to proceed uniformly by a suitable change of reaction of the liquor. Another safeguard which tanners have been forced to adopt, without understanding its mechanism, is so to regulate the reactions of both the tan liquors and the solution absorbed by the skin proteins just prior to tanning that the tanned and untanned portions of the skin protein do not tend to assume greatly different specific volumes.

The progress of the diffusion of the tan liquor into the skin is determined by cutting off a strip and observing the color of the freshly exposed portion. The raw portion is white and the tanned layers usually a deep brown. When the tannin has penetrated almost to the middle of the skin, it is customary to take the skins off from the sticks and pile them into vats known as *handlers* or *layers*. The name handler is used when the skins are handled from vat to vat at fre-

quent intervals until completely tanned. The name layer is used for the vats in which heavy hides are laid away for long periods, during which the tannin diffuses very slowly into the interior. Although hardly more than a week is consumed in the diffusion of the tan liquor into a light skin, months are required in some processes of sole leather manufacture.

Where great solidity is required, as in sole leather, it is not sufficient merely to convert all of the collagen into leather. The volume of the collagen fibers increases as more tannin combines with them. After the hides have become completely colored throughout, it is customary to treat them with very strong tan liquors with the object of getting as much tannin fixed as possible, and mechanical agitation of one kind or another is often employed. Usually the weight of sole leather is further increased by the incorporation of glucose and magnesium sulfate in the leather.

The Structures of Tanned Skins.

In the manufacture of leather for definite purposes, the choice of the kind of skin is of the greatest importance. By varying the nature of the tanning process, the properties of the leather can be varied, but not sufficiently to make one kind of skin suit all purposes. Advantage is taken of the variety of skins furnished by nature in order to simplify the tanning process itself.

Fig. 103 shows a vertical section taken from the butt of a steer hide tanned for sole leather. The natural solidity of this hide is so great that a heavy degree of tannage would not have been necessary in order to produce a leather suitable for shoe soles. This particular leather was heavily tanned with oak bark extract, but was not loaded with glucose and magnesium sulfate.

A section of vegetable tanned calf skin is shown in Fig. 143 of Chapter 14, where it was put for direct comparison with chrome tanned calf made from part of the same skin. It is interesting to compare its structure after tanning with that of calf skin in the fresh state, shown in Fig. 18 of Chapter 2. The leather is typical of the finest grade of finished shoe upper leather.

Fig. 104 shows a section of vegetable tanned sheep skin just as it came from the tan liquors. Note the great contrast which it presents to the leather made from steer hide or calf skin. The holes and empty spaces left by the wool and glands give the leather a sponginess that makes it unsuitable for many purposes. The upper layer is often split from the rest of the skin and used in bookbinding, for hat bands and for the linings of expensive shoes instead of cloth. Sheep skin leather is sometimes used as a substitute for kid leather in the manufacture of gloves, where its softness is an asset. The raw skin is shown in Fig. 28.

Fig. 105 is a section of vegetable tanned leather from the butt, or shell, of a horse hide. This is finished leather ready for use in the manufacture of the uppers of heavy, waterproof shoes. The raw

hide, at much lower magnification, is shown in Fig. 31. It will be noted that the leather has been split into layers through the portion known as the glassy layer, only the upper layer being used. The compactness of the fibers in the bottom third of the leather makes it waterproof and almost airtight. Leather from this part of the horse hide is known as Cordovan. The section should be compared with Fig. 145 of Chapter 14, which shows a section from the same butt which has been chrome tanned; the contrast is striking.

The peculiarity of the horse hide is that this compact fibrous structure is found only in the butt, the rest of the hide being very loose in texture. Fig. 106 shows a section taken from the same piece of leather as that shown in Fig. 105, but from a point further up the back beyond the boundary of the glassy layer. Its softness and sponginess has found for it a use in the manufacture of heavy gloves.

The section shown in Fig. 107 is that of a vegetable tanned hog skin. A section of the fresh skin is shown in Fig. 30. When the flesh side of the leather was shaved to make it smooth, the bottom of the pocket of the hair follicle was cut away, leaving the hole running right through the leather, as shown in the figure. This is typical of hog leathers; wherever there were bristles in the original skin, holes pierce the final leather. The roughness of the grain surface of the leather gives it a place in the manufacture of saddles, football covers, purses, etc.

Fig. 108 shows a vertical section of salmon leather taken directly from the vegetable tan liquors. It should be compared with the section of fresh skin shown in Fig. 36. The gap in the upper portion is the follicle once occupied by a scale. The structure of the leather makes it suitable for belt lacings.

The raspy feel of certain kinds of shark leather is explained by the section shown in Fig. 109. Shark leather has recently been tried for shoe uppers, in which case the hooks are removed prior to tanning. The fibrous structure resembles that of other fishes.

Fig. 110 shows a vertical section of vegetable tanned alligator skin. This type of leather finds an outlet in the manufacture of bags and cases. Fig. 111 shows a section of leather made from the skin of a horned toad. Although these skins are very small, they make very pretty doilies and fancy purses. In both the alligator and toad skins, the fibrous structure resembles that of the fishes.

A section of leather made from camel skin is shown in Fig. 112. It is remarkable for its compact structure, which would make it suitable for belting leather or for light soles. Figs. 113 and 114 show portions of the section of a vegetable tanned walrus hide and Figs. 115 and 116 show sections of the tanned hide of a hippopotamus.[1] The most remarkable thing about these hides is their great size. The actual thickness of the walrus leather was 24 millimeters and that of the hippopotamus leather 30 millimeters. In order to show the entire

[1] The hippopotamus, walrus, and camel leathers were very kindly furnished by Professor Douglas McCandlish of the University of Leeds, England.

Fig. 103.—Vertical Section of Steer Hide Leather.
(Sole leather.)

Location: butt.
Thickness of section: 40 μ.
Stain: none.
Tannage: vegetable.

Eyepiece: none.
Objective: 48-mm.
Wratten filter: H-blue green.
Magnification: 15 diameters.

Fig. 104.—Vertical Section of Unfinished Sheep Leather.

Location: butt.
Thickness of section: 30 μ.
Stain: none.
Tannage: vegetable.

Eyepiece: none.
Objective: 16-mm.
Wratten filter: H-blue green.
Magnification: 46 diameters.

Fig. 105.—Vertical Section of Horse Leather.
(Cordovan—from shell.)

Location: butt.	Eyepiece: none.
Thickness of section: 20 u.	Objective: 16-mm.
Stain: Daub's bismarck brown.	Wratten filter: H-blue green.
Tannage: vegetable.	Magnification: 70 diameters.

Fig. 106.—Vertical Section of Horse Leather.
(From spongy part of back near shell.)

Location: back.
Thickness of section: 20 μ.
Stain: Daub's bismarck brown.
Tannage: vegetable.

Eyepiece: none.
Objective: 16-mm.
Wratten filter: H-blue green.
Magnification: 70 diameters.

Fig. 107.—Vertical Section of Hog Leather.

Location: butt.
Thickness of section: 30 μ.
Stain: none.
Tannage: vegetable.

Eyepiece: none.
Objective: 16-mm.
Wratten filter: K3-yellow.
Magnification: 46 diameters.

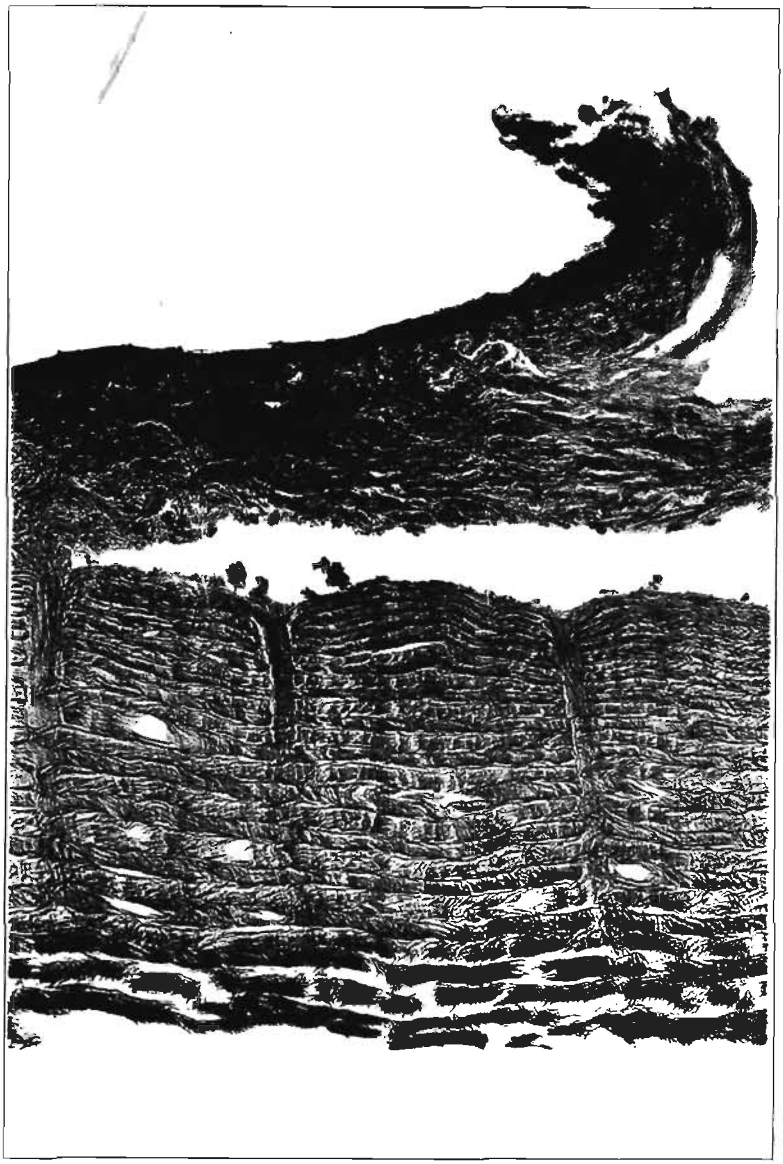


Fig. 108.—Vertical Section of Unfinished Salmon Leather.

Location: side.
Thickness of section: 20 μ.
Stain: none.
Tannage: vegetable.
Eyepiece: 5X.
Objective: 16-mm.
Wratten filter: B-green.
Magnification: 110 diameters.

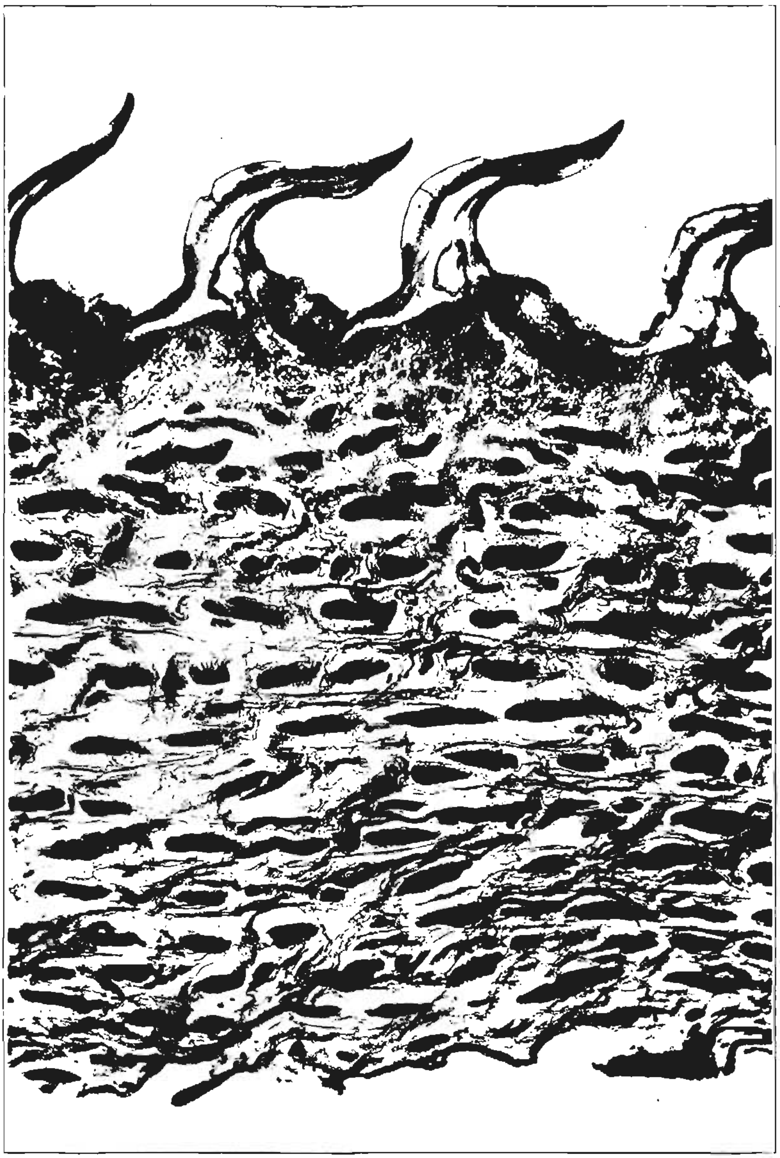


Fig. 109.—Vertical Section of Shark Leather.

Location: (?).
Thickness of section: 50 µ.
Stain: none.
Tannage: vegetable.

Eyepiece: 5X.
Objective: 16-mm.
Wratten filter: B-green.
Magnification: 75 diameters.

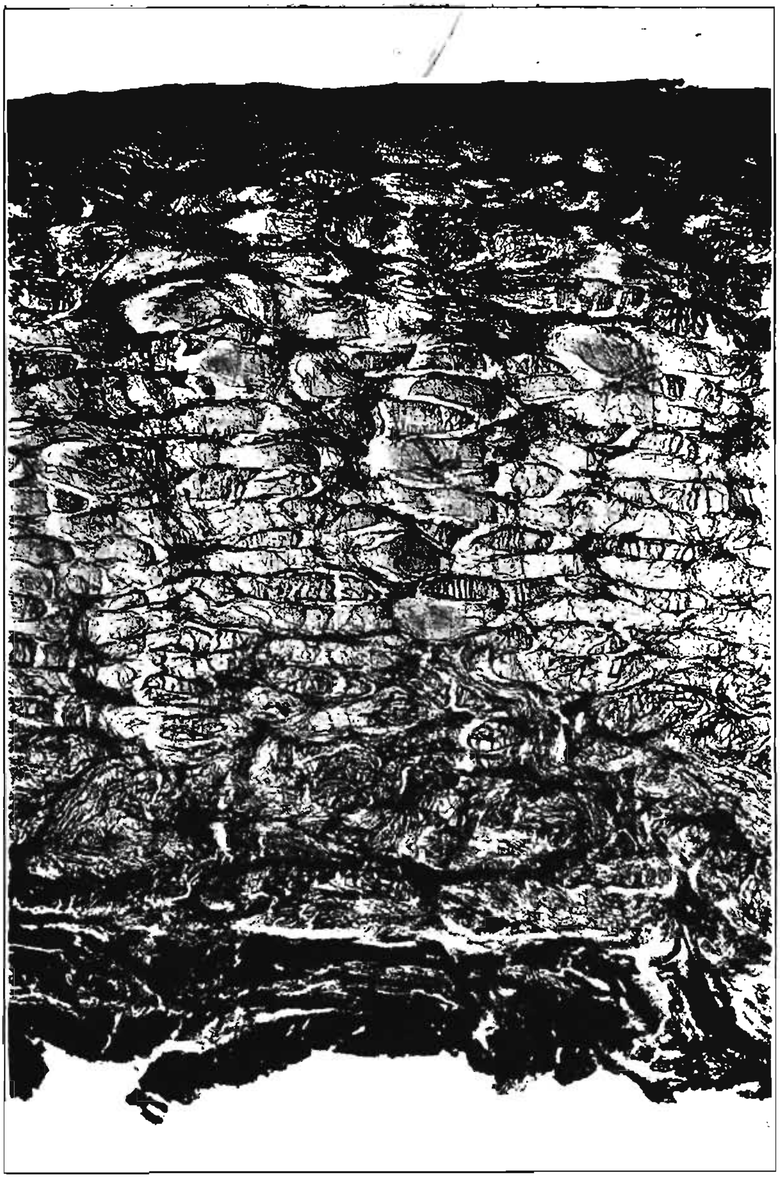


Fig. 110.—Vertical Section of Alligator Leather.

Location: back.
Thickness of section: 50 μ.
Stain: none.
Tannage: vegetable.

Eyepiece: none.
Objective: 16-mm.
Wratten filter: G-yellow.
Magnification: 45 diameters.

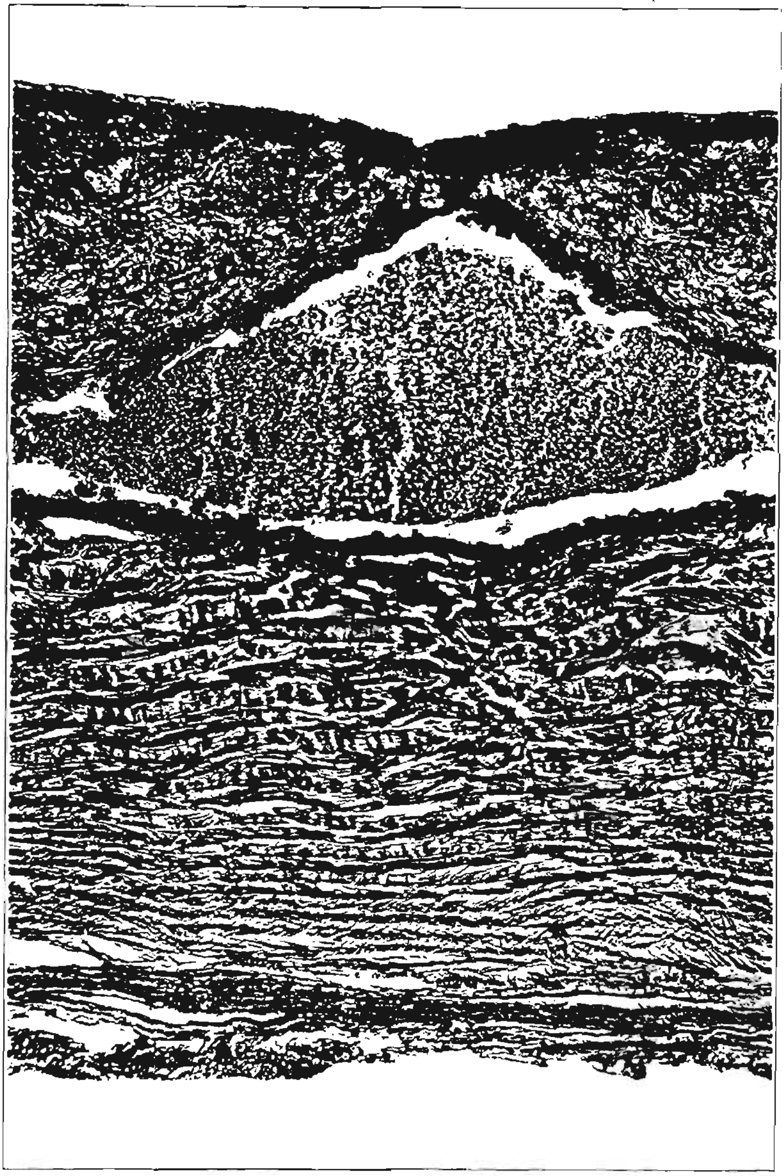


Fig. 111.—Vertical Section of Horned-Toad Leather.

Location: butt.	Eyepiece: 5X.
Thickness of section: 20 μ.	Objective: 8-mm.
Stain: none.	Wratten filter: H-blue green.
Tannage: vegetable.	Magnification: 220 diameters.

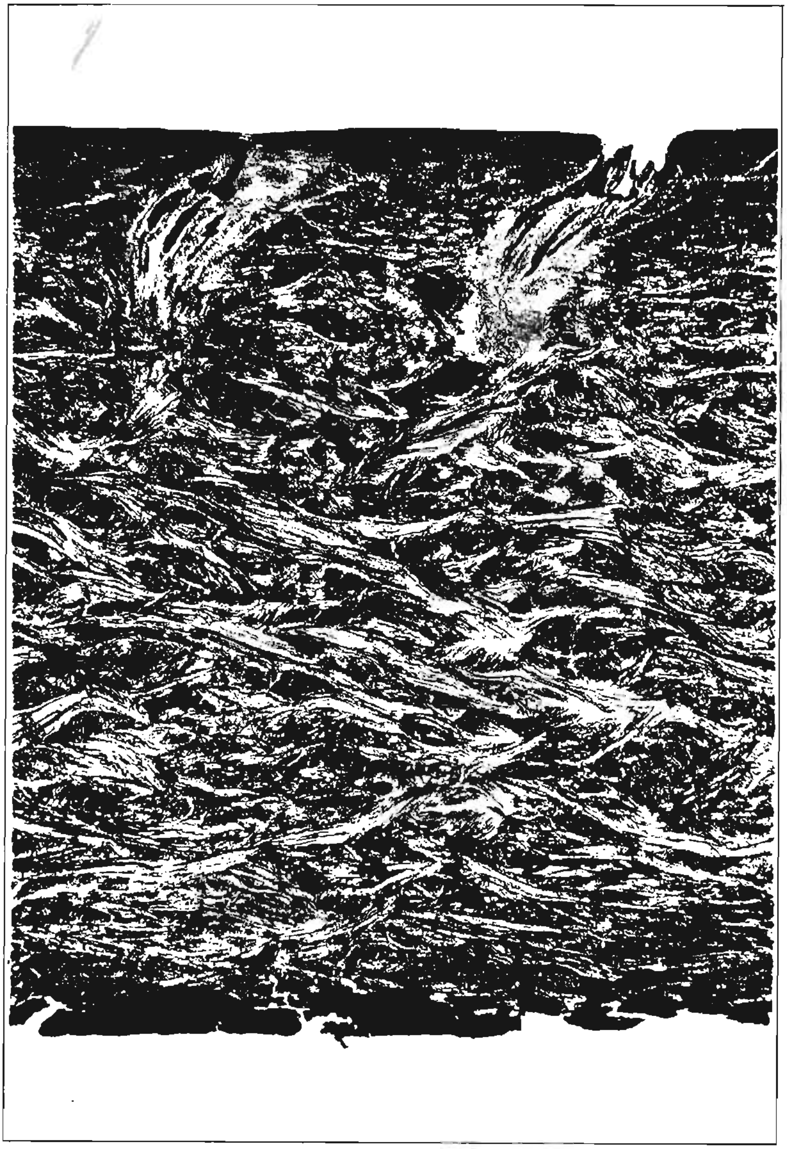
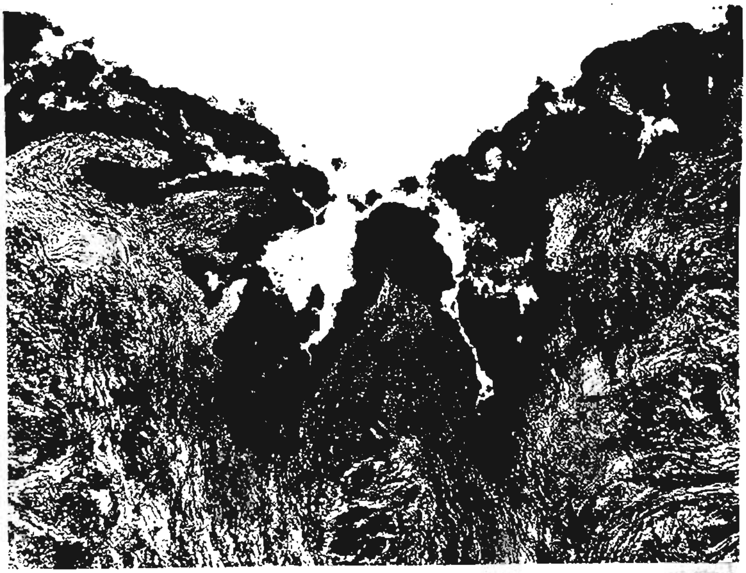


Fig. 112.—Vertical Section of Camel Leather.

Location: butt(?).
Thickness of section: 30 μ.
Stain: none.
Tannage: vegetable.

Eyepiece: none.
Objective: 32-mm.
Wratten filter: B-green.
Magnification: 30 diameters.



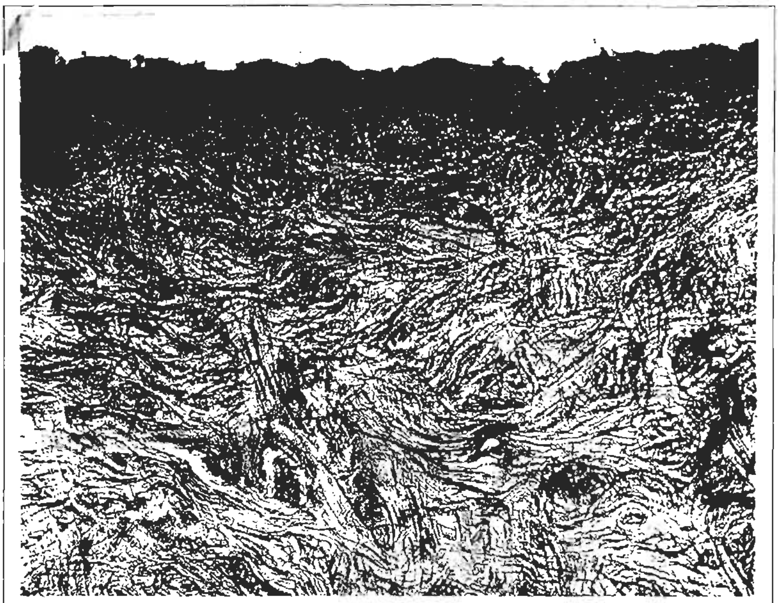
Portions of Vertical Section of Walrus Leather.

FIG. 113.—Region of Grain Surface.

FIG. 114.—Region 22 Millimeters Below Grain Surface.

Location: butt(?).
Thickness of section: 40 μ.
Stain: none.
Tannage: vegetable.

Eyepiece: 5X.
Objective: 16-mm.
Wratten filter: G-yellow.
Magnification: 68 diameters.



Portions of Vertical Section of Hippopotamus Leather.

FIG. 115.—Region of Grain Surface.

FIG. 116.—Region 28 Millimeters Below Grain Surface.

Location: butt(?).
Thickness of section: 40 μ.
Stain: none.
Tannage: vegetable.

Eyepiece: 5X.
Objective: 16-mm.
Wratten filter: G-yellow.
Magnification: 68 diameters.

thickness of the leather at 68 diameters, a picture about seven feet high would be required.

The walrus must be very sensitive to touch, if we may judge from the highly developed papillæ which protrude everywhere from the grain surface. In neither of these leathers were the roots of the hair removed and the fat cells surrounding the hair bulbs of the walrus were still intact as though the unhairing liquors had not penetrated that deeply. Except for the huge collagen fibers in the reticular layer, and the great size of the hide, the walrus hide resembles that of the common hog. It is interesting to compare the fibers of these leathers with those of the smaller skins, but the differences in magnification must be taken into consideration.

It has often been supposed that the tanning action consists of a coating of the skin fibers with tannin, but observations of sections under the microscope indicate that this is not the case. The outer surfaces of the skin act as filters, permitting only the soluble matter to pass into the interior, where it subsequently diffuses into the substance of the fibers, which assume a uniform color throughout when tanning is finally complete. In finished leather, contrary to what seems to be the general belief, we find no coating of the surfaces of the fibers nor any material precipitated in the spaces between them.

Rate of Diffusion of Tan Liquor into Gelatin Jelly.

The great length of time required to tan heavy leathers is due to the very slow rate of diffusion of the tannin into the interior of the hides. Because of the difficulty of measuring the extent of penetration of tan liquors into raw hides, studies of the rate of diffusion are usually made with tubes of gelatin jelly. Hoppenstedt[2] noted that different tanning extracts diffused into gelatin jelly at different rates, the order of increasing rate of diffusion being mangrove bark, quebracho, hemlock bark, algarobilla, valonia, oak bark, myrobalans, chestnut wood, gambier, divi-divi, sumac.

Later Thomas[2a] showed that the rate of diffusion of tanning extracts into gelatin jelly increases with the ratio of nontannin to tannin in the extract. For typical samples, he found the rate of diffusion increasing in the order quebracho, hemlock bark, larch bark, oak bark, chestnut wood, gambier, sumac, agreeing with the results obtained by Hoppenstedt. This is also the order for decreasing astringency of these materials, as ordinarily used. The same order is roughly borne out in experiments dealing with the rate of diffusion into cow hide.

The action of nontannins in increasing the rate of diffusion of tannins into skin may be explained as follows: Tannins and certain nontannins form compounds with collagen, but the collagen-tannin compound is very stable, while the collagen-nontannin compounds are

[2] Diffusion of Tannins through Gelatin Jelly. A. W. Hoppenstedt. *J. Am. Leather Chem. Assoc.* 6 (1911), 343.

[2a] Order of Diffusion of Tanning Extracts through Gelatin Jelly. A. W. Thomas. *J. Am. Leather Chem. Assoc.* 15 (1920), 593.

considerably dissociated. The nontannins, having a much smaller molecular weight than the tannins, diffuse more rapidly into the skin. When the slowly moving tannin reaches a point where it would combine with collagen, it cannot do so because the point is already occupied by nontannin. Tannin that would otherwise have combined with collagen near the surface of the skin is thus enabled to proceed into the interior and the measured rate of penetration is thereby increased. This action is more marked the greater the concentration of nontannin capable of combining with collagen. The collagen-tannin compound being much the more stable, tannin replaces nontannin as fast as the collagen-nontannin compound hydrolyzes.

According to the Procter-Wilson theory of tanning, to be discussed presently, the rate of tanning, and also of the combination of collagen with certain nontannins, can be decreased either by increasing the electrolyte concentration or by lowering the positive electrical charge which collagen possesses in acid solution, which can be accomplished by decreasing the acidity. We should therefore expect the constituents of a tan liquor, both tannin and nontannin, to penetrate skin more rapidly as the acidity of the tan liquor is decreased to the isoelectric point of collagen.

Thomas prepared a 5-per cent dispersion of gelatin in hot water containing 0.1 per cent ferric chloride and poured it into a series of test tubes to three-quarters of their capacity. When the dispersions had set to jelly, equal volumes of solutions of different extracts were poured on top of the jellies, which were then placed in an ice box. All of the extract solutions were made to contain 1 per cent of dry solid matter. Tannin and some nontannins react with ferric chloric giving very deep green or blue colors, which served to indicate the extent of the penetration. In 96 hours the gambier had penetrated 18.0 millimeters as against only 4.8 millimeters by the quebracho. It was, of course, the extent of penetration by certain nontannins that was measured, as these diffuse more rapidly than the tannin.

Wilson and Kern[3] treated a large volume of a dispersion of gelatin in dilute ferric chloride solution with tartaric acid until its pH value was reduced to 2.5, as determined by the hydrogen electrode. Equal portions were then treated with sodium hydroxide to give the desired pH values, which ranged from 2.5 to 11.0. Dilutions were such that the final dispersions contained 5 per cent of gelatin and 0.1 per cent of ferric chloride, as in the experiments of Thomas.

Solutions of gambier and quebracho extracts were treated with tartaric acid to give a pH value of 2.5. Equal portions were then treated with sodium hydroxide to give series of pH values the same as in the series of jellies. Each final liquor contained 1 gram of solid matter of the original extract per 100 cubic centimeters.

The gelatin dispersions were poured into test tubes and allowed to set. Onto each was poured a given volume of tan liquor having the same pH value as the jelly. Both the quebracho and gambier series

[3] Effect of Change of Acidity upon the Rate of Diffusion of Tan Liquor into Gelatin Jelly. J. A. Wilson and E. J. Kern. *J. Ind. Eng. Chem.* 14 (1922), 45.

were run in duplicate. They were kept in the ice box and examined at intervals for 96 hours. The extent of the diffusion of the tan liquors into the jellies is shown in Fig. 117, the measurements being taken after 96 hours. In each case the duplicate series were practically identical.

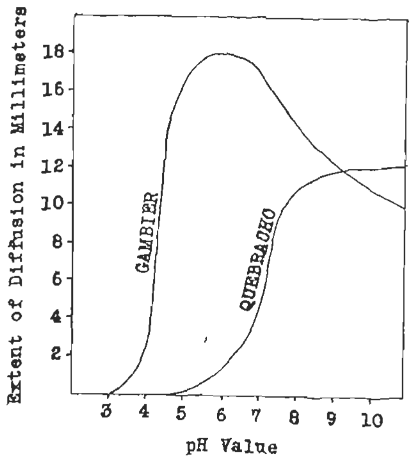


FIG. 117.—Rate of Diffusion of Tan Liquor into Gelatin Jelly as a Function of pH Value.

Gambier, which has a high *ratio of nontannin to tannin*, begins to penetrate at a pH value of 3.0 and reaches its maximum rate at pH = 6.0. Quebracho, on the other hand, scarcely shows any penetration until pH = 4.7, the isoelectric point of gelatin, is reached. At pH, values greater than 9, however, the quebracho liquor penetrates at the greater rate, possibly because of its higher tannin content.

Studies were also made of the effect of change of pH value upon the rate of diffusion of tan liquors into cow hide. With increasing pH values up to about 8, there is a distinct increase in rate of diffusion, but because of the flaccid nature of hide at pH = 8 it is difficult to make accurate measurements of the rate of diffusion. At pH values below 3 and above 11 the hide swells considerably and becomes rubbery and distorted.

Rate of Tanning as a Function of Time and Concentration of Tan Liquor.

An extremely important series of investigations of the nature of the vegetable tanning process has recently been begun by Thomas and Kelly, which promises to throw much light on the mechanism of this very complex process. Their first studies [4, 5] were devoted to the effects of time and concentration. In their preliminary experiments, portions of purified hide powder were shaken with definite quantities of unfiltered solutions of tanning extracts for stated lengths of time, washed free from soluble matter, and then analyzed for the purpose of determining the amount of tannin combined with a unit of hide substance. In the more concentrated liquors, however, an error was introduced by the occlusion of insoluble matter by the hide powder, which was included as combined tannin because it was not removed later by washing.

[4] Time and Concentration Factors in the Combination of Tannin with Hide Substance. A. W. Thomas and M. W. Kelly. *J. Ind. Eng. Chem.* 14 (1922), 292.
[5] The Concentration Factor in the Fixation of Tannins by Hide Substance. *Ibid.* (1923); (advance copy).

In their most recent work, Thomas and Kelly adopted a method practically identical with the modified Wilson-Kern method of tannin analysis described in Chapter 12, except for the fact that no attempt was made to detannize the various solutions completely. All tan liquors were centrifuged and filtered and only the clear filtrates used in the experiments. The use of filtered liquors with hide powder gave results which were more uniform and which probably represent actual tanning conditions more closely, since the surfaces of the whole skin act as filters, permitting only the soluble matter to come into contact with the great bulk of the skin protein.

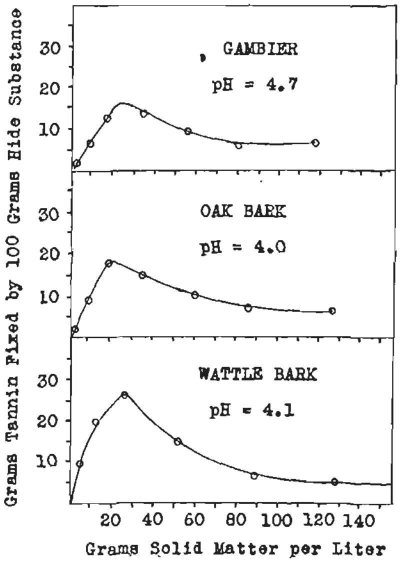


FIG. 118.—Rate of Tanning as a Function of the Concentration of Tan Liquor. Time, 24 hours.

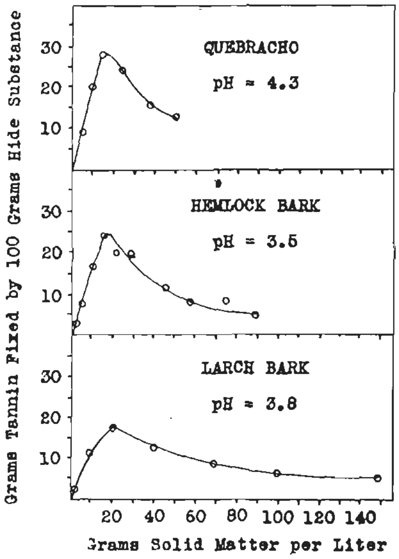


FIG. 119.—Rate of Tanning as a Function of the Concentration of Tan Liquor. Time, 24 hours.

Portions of purified hide powder equal to 2 grams of anhydrous substance were shaken with 100 cubic centimeters of tan liquor of the desired concentration and for fixed intervals of time. The powder was then washed until the wash water no longer gave a dark color upon the addition of a drop of ferric chloride solution. It was found that the ferric chloride test is capable of detecting 1 part in 75,000 of either gallic acid or pyrogallol. The powders, freed from soluble matter, were dried in a current of warm air and then completely dried in the oven. The increase in weight of the absolutely dry material was taken as the amount of tannin fixed by 2 grams of hide powder.

Figs. 118 and 119 show how the rate of tanning varies with increasing concentration of solutions of quebracho, hemlock bark, larch

bark, gambier, oak bark, and wattle bark extracts. The mild action of gambier, as contrasted with the astringency of quebracho, is graphically shown by the steep rise of the quebracho curve compared

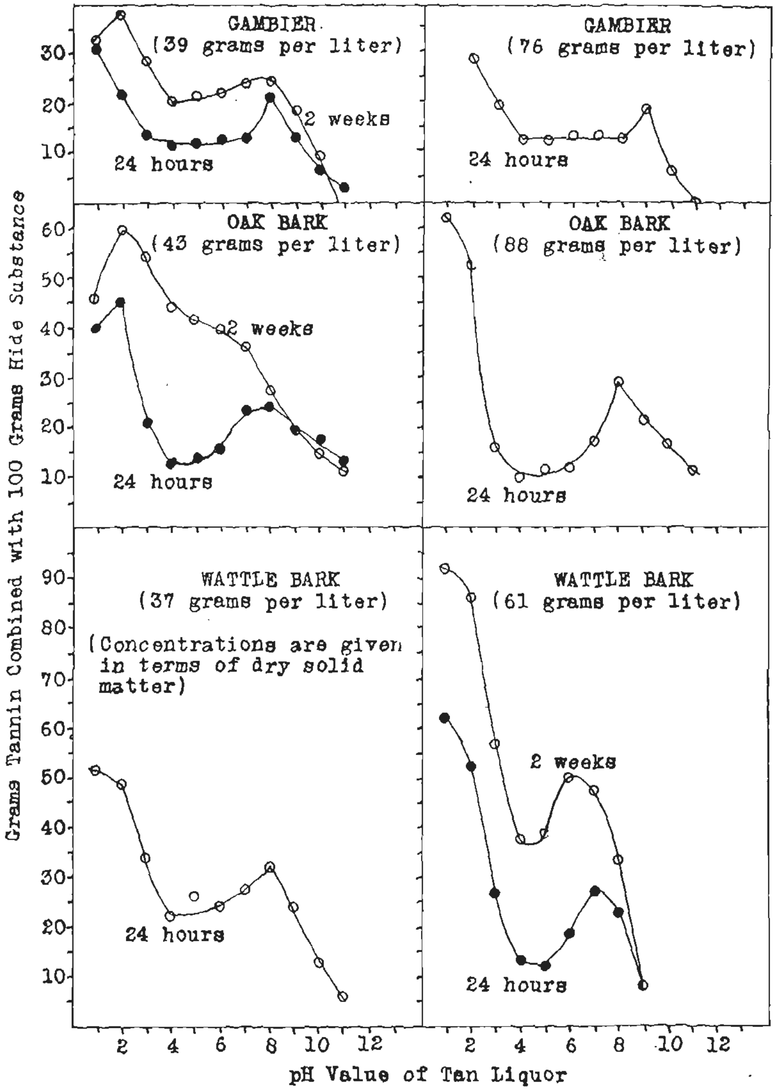


FIG. 120.—Rate of Tanning as a Function of pH Value.

with that of the gambier series. It is remarkable that all extracts give curves of similar shape and having points of maximum at the relatively low concentrations ordinarily used in practice. Thomas and

Kelly showed definitely that the rise and fall in the curves cannot be attributed to variations in hydrogen-ion concentration, but is due to the increasing concentration of the other constitutents of the tan liquors.

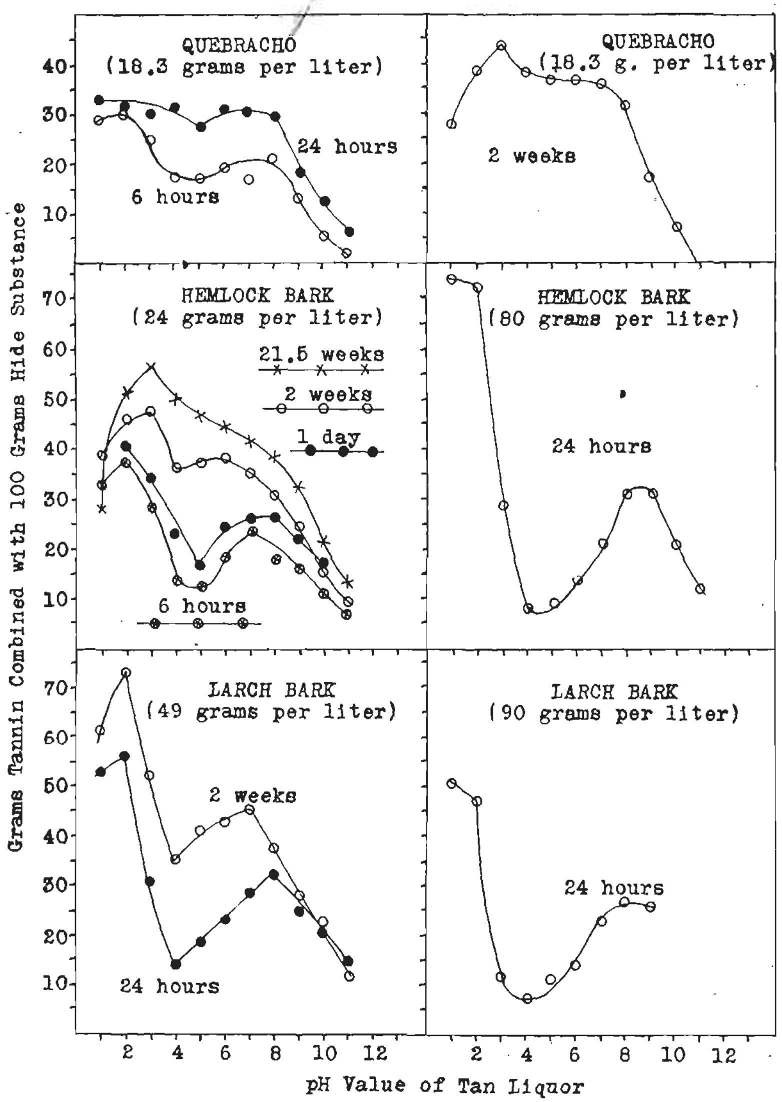


FIG. 121.—Rate of Tanning as a Function of pH Value.

One explanation given for the appearance of points of maximum in the curves is that the rate of combination of tannin and hide substance increases so rapidly, with increasing concentration of tan liquor,

that it soon reaches a point where the surfaces of the hide fibers quickly become so heavily tanned that they are rendered less permeable to the tannin remaining in solution. The interior of the fibers are thus prevented from tanning so rapidly, which accounts for the smaller amount of tannin fixed by the hide powder in the stronger solutions. Another explanation is furnished by the work of Thomas and Foster,[6] who observed that the electrical difference of potential at the surface of tannin particles decreases with increasing concentration of tan liquor. This would lessen the attraction between the tannin particles and the protein jelly and thus cause a decrease in the rate of combination. This seems the more probable explanation because a greater rate of diffusion of tan liquor into skin is obtained in practice by using more concentrated solutions. The curves represent the resultant of two effects: the increasing concentration of tannin tends to cause an increase in the rate of tanning and the increasing concentration of nontannin tends to cause a decrease in the rate of tanning. The point of maximum represents the point at which the effect of the increasing concentration of nontannin becomes greater than that of the tannin.

These curves are in agreement with the findings of a number of investigators that highly concentrated tan liquors are very much less astringent than those of moderate concentrations. In practice, the degrees of astringency of tan liquors seem to follow curves similar to those in the figures. The use of concentrated liquors in tanning has been suggested by Seymour-Jones[7] and by Enna,[8] but the idea seems not to have been widely adopted, probably because it introduces complications in the later processes not easily overcome without some loss in quality of the finished leather.

Rate of Tanning as a Function of pH Value.

Thomas and Kelly[9] next turned their attention to the effect of the pH value of tan liquors upon the fixation of tannin by hide substance. The procedure adopted was the same as in the studies of the effect of concentration. In each case the pH value of the tan liquor, as determined by the hydrogen electrode, was adjusted to the desired value by the addition of sodium hydroxide or hydrochloric acid. Figs. 120 and 121 show the effect of change of pH value on the rate of the tanning of hide powder by solutions of quebracho, gambier, oak bark, wattle bark, hemlock bark, and larch bark extracts. The curves contain a mine of information that requires careful study.

The most elaborate set of curves is that for hemlock bark extract.

[6] The Colloid Content of Vegetable Tanning Extracts. A. W. Thomas and S. B. Foster. *J. Ind. Eng. Chem.* 14 (1922), 191.

[7] Rapid Tanning of Sole Leather. Alfred Seymour-Jones. *J. Soc. Leather Trades' Chem.* 1 (1917), 2.

[8] Rapid Tannage. Fini Enna. *Ibid.,* 1 (1917), 36.

[9] The Hydrogen-Ion and Time Factors in the Fixation of Tannins by Hide Substance. A. W. Thomas and M. W. Kelly. *Ind. Eng. Chem.* (1923); Dissertation, Miss Margaret W. Kelly, Columbia University, 1923.

which may be discussed as typical. In the concentration experiments, a tan liquor containing 24 grams of solid matter per liter gave a much greater rate of tanning than one containing 80 grams per liter, but the curves in Fig. 121 show that this is dependent upon the pH value; at pH = 5, the more dilute solution tans at the greater rate, while at 2 and at 8, the more concentrated solution tans at the greater rate.

In tanning for 24 hours, there is a steep rise in all curves to the left of pH = 5, which is exactly what one would expect, knowing that the positive electrical charge on collagen increases as the pH value falls from the isoelectric point and that the tannins are negatively charged at pH values higher than 2. In some cases a falling off in rate of tanning as the pH value drops below 2 is noticeable, but it must be remembered that the great tendency for collagen to swell and to hydrolyze at high acidities makes it difficult to get reliable data at pH values as low as 2.

The most curious parts of the curves are those between the pH values 5 and 8. Since tannin particles are negatively charged in this region, the question that naturally arises is the possibility that the collagen may become increasingly positive with rise of pH value from 5 to about 8. This might seem an absurd view were it not for the two points of minimum plumping of calf skin found by Wilson and Gallun and shown in Fig. 73 of Chapter 9. Here it was suggested that collagen undergoes a change of form, possibly an internal rearrangement, in passing from an acid to an alkaline solution and that the two points of minimum, at pH = 5.0 and at pH = 7.7, represent the isoelectric points of the two forms. We may refer to collagen stable in acid solution as form A and collagen stable in alkaline solution as form B. As the pH value is increased from 5.0 to 7.7, if the conversion of form A into form B proceeds at a greater rate than the formation of negatively charged ions of form A, then we should expect the net charge on the collagen structure to become increasingly positive, which would result in an increased rate of tanning.

The question was raised in discussion as to whether any fixation of tannin actually took place at pH values below 2 and above 8. In all of the experiments described, the powders were washed with distilled water immediately after being taken from the tan liquor. Distilled water usually has a pH value of about 5.8, due to dissolved carbonic acid, and this would tend to make the pH value of the solution absorbed by the collagen jelly approach the value 5.8 before it was all washed out and the observed fixation of tanning might have occurred during the washing rather than during the shaking with tan liquor. Thomas and Kelly showed, however, that fixation actually does take place at pH values below 2 and above 8.

They prepared a solution of wattle bark extract containing 40 grams of solid matter per liter and hydrochloric acid to bring the pH value to 0.87. Four portions of hide powder were tanned with this solution for 24 hours in the prescribed manner and then two were

washed with distilled water and two with a hydrochloric acid solution having a pH value of 0.87 until no more tannin could be extracted. The latter two were then washed free from hydrochloric acid with distilled water. The two powders washed with the acid solution were found to contain an average of 0.739 gram tannin combined with the original 2 grams of hide powder against 0.987 gram tannin for the powders washed with distilled water. This shows that, although washing with distilled water causes an increase in combined tannin found, there is actually a fixation of tanning taking place at pH = 0.87.

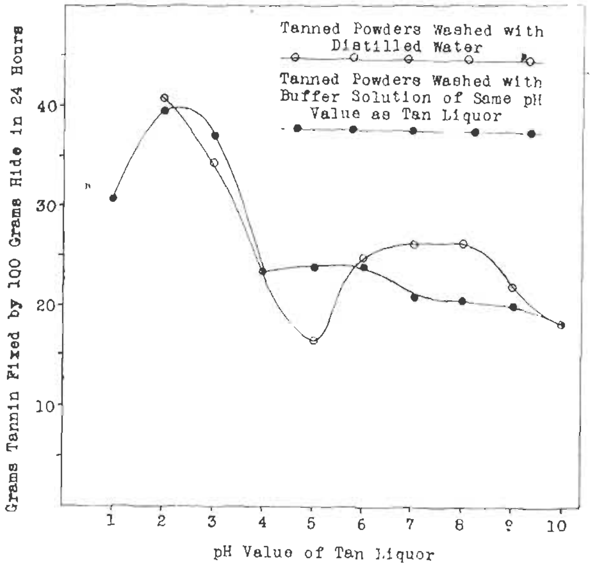


FIG. 122.—Showing the Rate of Tanning as a Function of pH Value and also the Effect of Washing the Tanned Powders with Buffer Solutions having the Same pH Value as the Tan Liquor Used in Tanning.

They then prepared two series of solutions of hemlock bark extract, containing 24 grams of solid matter per liter and having pH values ranging from 1 to 10, as determined by the hydrogen electrode. Portions of hide powder were tanned in each series for 24 hours in the prescribed manner and then the powders of one series were washed with distilled water, while those of the other were washed free from soluble tannin with solutions having the same pH values as the liquors in which the powders were tanned. For pH values of 4 or less, the solutions used for washing contained only hydrochloric acid; for pH values from 5 to 9, they were made from M/15 sodium phosphate adjusted to the desired pH value with HCl or NaOH; for pH = 10, a solution of sodium hydroxide was used. The final washing was done with distilled water. The results are shown in

Fig. 122. The two curves are not identical, but show plainly that tannin combines with hide substance at all pH values from 1 to 10. Where a buffer solution was used to wash the hide powder tanned at pH = 5, a greater fixation of tannin occurred. Salts at low concentration have the property of increasing the fixation of tannin at pH = 5, as will be shown later.

Stability of the Collagen-Tannin Compound at Different pH Values.

While studying the action of solutions of acid and alkali upon leather previously freed from water soluble matter, Wilson and Kern[10] found that tannin was extracted by dilute solutions of alkali, but not of acid. In an attempt to locate the pH value at which the collagen-tannin compound begins to hydrolyze, they performed the following experiment. A large amount of purified hide powder was tanned with quebracho extract at a pH value of 4.6, washed free from all soluble matter with distilled water, and then dried. Seven large reservoirs of buffer solutions were prepared by making up solutions of tenth-molar phosphoric acid with sodium hydroxide to produce the pH values 5, 6, 7, 8, 9, 10, and 11, respectively. Eight-gram portions of the tanned powder were put into Wilson-Kern extractors[11] and extracted with 4 liters of buffer solution, taking just 6 hours for all of the solution to percolate through the tanned powder. Each portion was extracted with a solution of different pH value. The extracted powders were washed free from buffer solution with distilled water and were then dried and analyzed for comparison with the original powder. All extracts were brought to a pH value of 4 and then tested for tannin with the gelatin-salt reagent. The buffer solutions extracted only negligible amounts of nitrogen from the powders. The results are shown in Table XXXII.

TABLE XXXII.

Analyses of Tanned Hide Powder Before and After Washing with Solutions of Different pH Values.

	Before washing	After washing with solution of pH = 5	6	7	8	9	10	11
Ash	0.2	0.4	0.5	0.4	0.6	0.3	0.5	0.4
Hide substance (N x 5.62)	84.2	83.9	83.9	83.9	84.2	84.7	84.9	85.3
Tannin (by difference)	15.6	15.7	15.6	15.7	15.2	15.0	14.6	14.3
Per cent of total tannin extracted	....	none	none	none	2.6	3.8	6.4	8.3
Test for tannin in extract	....	neg.	neg.	neg.	pos.	pos.	pos.	pos.

Leather tanned at pH = 4.6 is apparently resistant to hydrolysis by solutions having pH values up to some point between 7 and 8, but is at least partially hydrolyzed, and with increasing speed, as the

[10] Stability of the Hide-Tannin Compound at Different pH Values. J. A. Wilson and E. J. Kern. Presented before the Leather Division of the American Chemical Society, Sept. 6, 1922.

[11] For description, see *J. Ind. Eng. Chem.* 13 (1921), 772.

pH value is increased above 8. This adds some weight to the suggestion that 7.7 represents the isoelectric point of one form of collagen. But, taken in conjunction with the finding of Thomas and Kelly that collagen and tannin form stable compounds at pH values greater than 8, it also supports their view that the collagen-tannin compound formed in alkaline solution is different from that formed in acid solution, which will be made clearer when their later experiments are described.

Effect of Neutral Salts upon the Rate of Tanning.

The effect of the concentration of sodium chloride or sulfate upon the rate of tanning of hide powder by solutions of gambier and hemlock extracts, at different pH values, has recently been studied by Thomas and Kelly.[12] In each test, 100 cubic centimeters of tan liquor, a weighed amount of salt, and the equivalent of 2 grams of water-free hide powder were put into a bottle and shaken, in a rotating box, for 24 hours. The contents were then transferred to a Wilson-Kern extractor, filtered, and washed until the washings gave no coloration with ferric chloride solution. The tanned powders were then dried in a vacuum at 100° C. and weighed, the increase in weight of the dry powder being taken as tannin fixed.

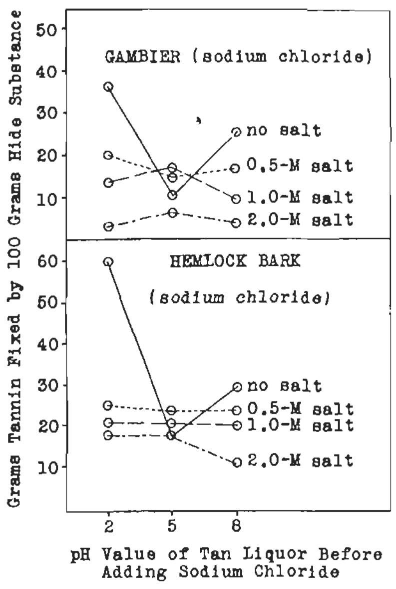


FIG. 123.—Effect of Sodium Chloride and pH Value upon the Rate of Tanning. Time, 24 hours.

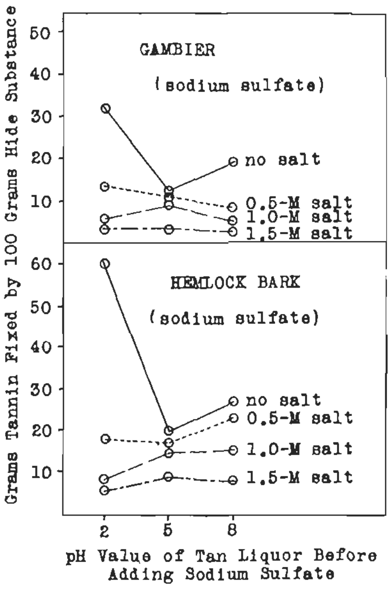


FIG. 124.—Effect of Sodium Sulfate and pH Value upon the Rate of Tanning. Time, 24 hours.

[12] The Influence of Neutral Salts upon the Fixation of Tannins by Hide Substance. A. W. Thomas and M. W. Kelly. *Ind. Eng. Chem.* (1923); (advance copy).

In order to guard against including as fixed tannin any matters rendered insoluble by the added salt, blanks were run leaving out the hide powder and corrections were made where necessary.

The insoluble matter of the extracts was first removed by centrifuging strong solutions, which were then diluted to contain 40 grams of solid matter of the tanning extract per liter, after adjusting the pH value to 2, 5, or 8, by addition of hydrochloric acid or sodium hydroxide.

The effect of sodium chloride is shown in Fig. 123 and that of sodium sulfate in Fig. 124. At pH = 2, both salts retard tanning to a very considerable extent, although sodium sulfate is always much more effective in this respect than sodium chloride. In each case the extent of the retardation is greater the higher the concentration of salt. At pH ≐ 8, the action of the salts is similar, but less pronounced. At pH = 5, the action is still less pronounced and is even reversed by concentrations of sodium chloride less than twice molar, which seem to cause an increase in rate of fixation of tannin.

The marked reduction in the rate of tanning at pH = 2 exerted by the salts is probably due primarily to the reduction of the electrical differences of potential between the collagen jelly and the liquor on the one hand and between the liquor and the surface film surrounding the tannin particles on the other. The potential difference between collagen jelly and liquor is probably at its maximum value in the vicinity of pH = 2 and, consequently, the depressing action of salt should be greatest at this point. According to the Procter-Wilson theory of tanning, a diminution in this potential difference must result in a decrease in rate of tanning. The greater effect of sodium sulfate may be attributed to the divalent sulfate ion, as explained in Chapter 5.

With the decreasing potential difference between the liquor and the surface film of solution in contact with the tannin particles, there would be an increasing tendency for the tannin particles to form aggregates and finally to precipitate out, further decreasing the rate of combination of tannin with collagen.

The effect of hydration of the added salt is to remove water from the rôle of solvent, as explained in Chapter 4, and this would cause a virtual increase in concentration of tannin. Thomas and Kelly point out that opposed to this, within certain limits, would be the tendency for the salt to cause an aggregation of the particles of tannin. These opposing actions may explain the behavior of sodium chloride at pH = 5. At this point the potential difference between the collagen jelly and the liquor would be near its minimum value and hence would be but little affected by the salt. The effects of hydration and of aggregation would therefore be much more pronounced at this point, and Thomas and Kelly suggest that the increase in rate of tanning by molar and half-molar sodium chloride may be due to the hydration effect and the decrease in rate of tanning by the stronger sodium chloride solution and the sodium sulfate solutions to the aggregation factor. They are continuing their studies of the action of salts upon the vegetable tanning process.

Degree of Plumping of Skin as a Function of Concentration of Acid and Salt in Tan Liquors.

Tanners of heavy leathers usually attach much importance to the degree to which the skin is swollen, or plumped, during the tanning operation. It is generally assumed that greater yields of leather are obtained when the skin is tanned in a highly plumped condition. If the plumping by means of acid is carried to excess, however, the skins will be ruined. The first sign of danger in this direction is a wrinkling and reticulation of the grain surface of the skin. A rapid tanning of the surfaces of the skin follows, rendering them almost impermeable to the tannin remaining in solution, and the fibers in the interior remain raw and swell considerably, assuming a glassy appearance. If left long in this condition, especially in warm liquors, the collagen hydrolyzes and the skin is damaged beyond hope of recovery.

TABLE XXXIII.

Degree of Plumping of Calf Skin Produced by Tan Liquor Containing 25 Grams of Oak Bark Extract per Liter and Lactic Acid and Sodium Chloride as Shown in the Table.

Moles per Liter Lactic acid	Moles per Liter Sodium chloride	Gauge Readings in MM. (average of triplicates) Initial	Final	Ratio *	Final pH Value at 25° C.
None	None	1.346	2.150	1.60	4.63
0.0025	"	1.411	2.343	1.66	3.94
0.0050	"	1.383	2.699	1.95	3.74
0.010	"	1.433	3.842	2.68	3.47
0.025	"	1.470	4.564	3.10	3.05
0.050	"	1.360	4.497	3.31	2.81
0.100	"	1.434	5.100	3.56	2.52
"	0.05	1.456	4.522	3.11	2.49
"	0.10	1.458	3.918	2.69	2.47
"	0.25	1.461	3.483	2.38	2.43
"	0.50	1.420	2.182	1.54	2.37

* This is a measure of the degree of plumping.

Wilson and Gallun [13] studied the effect of acids and salts upon the plumping of calf skin in tan liquors, using their method, which is described in Chapter 8. The effect of lactic acid and of sodium chloride upon the degree of plumping of calf skin in a solution of oak bark extract is shown in Table XXXIII and in Figs. 125 and 126.

For this experiment a piece was selected from the butt of a calf skin, after liming, unhairing, and washing, of as nearly uniform thickness as possible and cut into squares having a side of about 2 centimeters. These were delimed by washing with several changes of 0.01-molar hydrochloric acid containing 10 per cent of sodium chloride, then kept over night in a saturated solution of sodium bicarbonate containing 10 per cent of sodium chloride, washed thoroughly, and

[13] Direct Determination of the Plumping Power of Tan Liquors. J. A. Wilson and A. F. Gallun, Jr. *Ind. Eng. Chem.* 15 (1923), 376.

finally bated for 5 hours at 40° C. in a solution of 1 gram per liter of pancreatin, having a pH value of 7.6. The pieces were then washed for 24 hours in running tap water and were kept under distilled water in a refrigerator at 7° C. until used. The resistance to compression of each piece of skin was measured by means of a Randall & Stickney thickness gauge with a flat, metal base, upon which the piece of skin was placed, and a plunger, having a circular base 1 square centimeter in area, capable of pressing on the surface of the skin under constant pressure. The gauge reading was taken, in every case, exactly two minutes after dropping the plunger onto the skin.

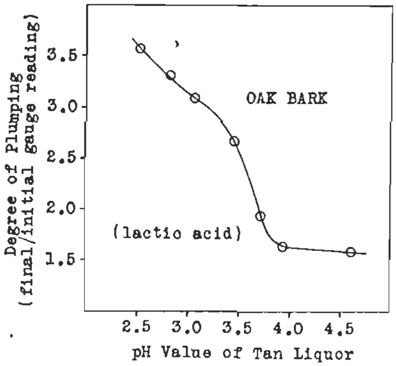


FIG. 125.—Effect of pH Value of Tan Liquor upon Degree of Plumping of Calf Skin.

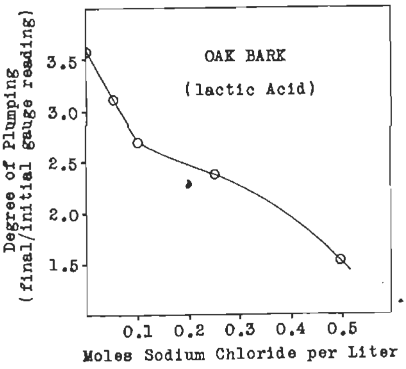


FIG. 126.—Effect of Sodium Chloride upon Degree of Plumping of Calf Skin in Tan Liquor Acidified with Lactic Acid.

Eleven tan liquors were prepared as indicated in Table XXXIII. The gauge readings of pieces of the standard skin were taken and they were then shaken with water to bring them back to their normal shape, after being compressed in the gauge. They were then put into the tan liquors and allowed to remain there for 24 hours at 20° C. The final gauge readings were then taken. In each case 3 pieces of skin were put into 100 cubic centimeters of tan liquor and the agreement between the triplicate determinations was satisfactory. The degree of plumping caused by the liquor is measured by the ratio of the final to the initial gauge reading.

The actions of the acid and the salt are not exactly the same as they would be in pure water, but are complicated by the tanning action of the liquor, which decreases the swelling power of the skin. The general tendency of the acid, nevertheless, is to swell the skin and the action of the salt to counteract this swelling.

McLaughlin and Porter[14] made a rather interesting study of the change in weight of limed steer hide during immersion in tan liquors

[14] On the Swelling and Falling of White Hide in Vegetable Tan Liquors. G. D. McLaughlin and R. E. Porter. *J. Am. Leather Chem. Assoc.* 15 (1920), 557.

of various compositions. Unfortunately the pH values of the liquors were not determined and, in many cases, it is not clear how much of the change observed is due to variation of hydrogen-ion concentration.

Rapid Tannages.

Numerous accounts appear in the literature of attempts to hasten the tanning process, especially for heavy leathers. But few of these have yet developed to a point where the mechanism of the process is well defined. In many cases, it appears likely that the added accelerator acts only indirectly by bringing about a more favorable reaction of the tan liquor itself.

One process for hastening tanning that seems, on the face of it, to merit further investigation is that described by Cross, Greenwood, and Lamb.[15] In the course of investigations on the hemi-celluloses of seed endosperms, the authors studied their compounds with tannin, which may be made to form apparently homogeneous jellies. From previous experience in the dyeing of silk, the authors conceived the idea of controlling the astringency of the tannin by using it in the form of a compound with the hemi-cellulose. They found that the use of "gum tragasol" in conjunction with the tannin solution caused a very rapid penetration of tannin into the skin. Complete penetration of very thick hides was obtained in two or three days, although the reduced rate of combination between collagen and tannin required the keeping of the hides in the liquor for a somewhat longer time than this.

A similar type of process is that proposed by Turnbull and Carmichael[16] in which the tanning materials are dissolved in a jelly formed of a starch solution.

Another process intended to hasten the tanning of heavy hides is that of C. W. Nance[17] and known as the vacuum process. The hides are put into a tank, which is then evacuated to a pressure of 0.5 lb. per square inch. The temperature is then gradually raised to the point at which water boils at this pressure. The tan liquor is introduced and the temperature allowed to fall slowly to permit the hide to absorb tan liquor to replace the water lost by boiling. By a proper regulation of temperature and pressure as well as concentration of tan liquor, it is claimed that an enormous reduction in time of tanning can be effected.

Attempts have been made at various times to hasten the tanning process by the application of an electric current. The hides are placed between carbon electrodes and the current turned on; in moving towards the anode, the tannins are thus made to penetrate the hide. Rideal and Evans[18] pointed out that to get good results the conductivity of

[15] Colloidal Tannin Compounds and Their Applications. C. F. Cross, C. V. Greenwood, and M. C. Lamb. *J. Soc. Dyers Colourists* (1919), 35, 62.

[16] A. Turnbull and T. B. Carmichael. British Pat. 110,470, Feb. 24, 1917.

[17] U. S. Pat. 1,065.168, June 17, 1913.

[18] Some Experiments on the Theory of Electro-Tanning. E. K. Rideal and U. R. Evans, *J. Soc. Chem. Ind.* 32 (1913), 633.

the liquor must be very low and that the cathodes should be made of carbon and the anodes of copper. Williams[19] found that a direct current causes a rapid destruction of pure gallotannic acid, which did not take place when an alternating current was used. Following the presentation of Rideal and Evans' paper, J. G. Parker said that he had experimented with electrical tanning and doubted that it had any advantages over systems not involving the use of the electric current. At any rate, it has not been adopted very widely as yet.

Much attention has been paid recently to the effect of adding organic compounds containing sulfonic groups to vegetable tan liquors upon the rate of penetration of the tan liquor into the hide. Among the materials commonly used may be mentioned the lignosulfonic acids obtained from the so-called sulfite cellulose, a by-product in the manufacture of paper from wood pulp, and also the synthetic products known as syntans, discovered by Stiasny, which will be discussed in Chapter 15. These materials act much like certain nontannins naturally occurring in vegetable tanning materials in lessening the astringency of the liquors and hastening the penetration of tannin into the skin. Apparently they have lower molecular weights than the tannins, which enable them to diffuse into the skin more rapidly. Since they actually combine with the collagen, they retard the combination of the true tannins with collagen, which thus permits tannin to diffuse into the interior that would otherwise have combined with collagen at the outer surface. This makes them valuable materials to use in the early stages of tanning. Whether or not the sulfonic groups which they possess are harmful for some kinds of vegetable tanned leathers has been the subject of debate, but has not yet been clearly settled.

The acid character of these sulfonic groups gives the liquors a very low pH value, which in turn causes a lightening of the color of both the liquors and the leather. In some cases there seem to be combinations between the tannins and the sulfonic compounds, resulting in compounds less easily precipitable than the original tannins. The synthetic materials seem also to cause a reduction of some of the more highly oxidized tannins, which may explain in part the lesser tendency of certain mixtures to precipitate upon the addition of acid.

Theory of Tanning.

Until it became possible to treat the chemistry of the proteins in a quantitative manner, there was little hope of developing a quantitative theory of tanning. Numerous attempts to determine the relative combining weights of gelatin and tannin led only to variable and often apparently contradictory results because of the failure to appreciate the existence of uncontrolled variable factors. A review of the older literature on theories of tanning would be of little more than historical value.

The modern theories of tanning are following the general trend of

[19] Inquiry into Electrical Tannage. O. J. Williams. *Collegium* (1913), 76.

development of the chemistry of the proteins. One school of thought treats the theory of tanning from the viewpoint of the physical chemistry of the proteins and the other from that of organic chemistry.

Procter-Wilson Theory.

The line of investigation of the physical chemistry of the proteins started by Procter led naturally to the conception of the mechanism of tanning formulated by Procter and Wilson.[20] The work leading to the formulation of this theory is given in detail in Chapter 5 and need not be repeated here. When in equilibrium with a tan liquor having a pH value lying in the range 2 to 5, collagen may be looked upon as constituting an aggregate of complex cations balanced by much simpler anions held in the solution immediately in contact with the collagen structure by the same forces that hold all oppositely charged ions together. We may assume that the collagen composing a hide fiber has a structure corresponding to that of gelatin when set to a jelly.

The theory may be pictured very simply by considering a piece of skin in contact with a solution containing only tannin and the acid HA. When equilibrium is established between the collagen and the acid, in the tan liquor let

$$x = [H^+] = [A']$$

and in the jelly phase of the collagen let

$$y = [H^+]$$

and $z = [CH^+]$ (i.e., concentration of collagen cation)

whence $[A'] = y + z.$

The equilibrium conditions are exactly analogous to those described for gelatin, from which it is apparent that there will be an electrical difference of potential between the jelly phase and the external solution expressible quantitatively by

$$E = \frac{RT}{F} \log \frac{y}{x} = \frac{RT}{F} \log \frac{-z + \sqrt{4x^2 + z^2}}{2x}.$$

Each tannin particle is negatively charged and, consequently, must have associated with it an equivalent number of cations held in the solution immediately in contact with the particle, which we may call the surface film for convenience, although it makes no difference to the theory whether the tannin particle is solid, like a gold particle, or a jelly particle capable of absorbing solution. Let the concentration of these cations be represented by z_1 and the concentration of the anion A′ in the surface film by y_1; the total concentration of cation then equals $y_1 + z_1$. The electrical difference of potential between the surface film and bulk of solution then equals

[20] Theory of Vegetable Tanning. H. R. Procter and J. A. Wilson. *J. Chem. Soc.* 109 (1916), 1327.

$$E_1 = \frac{RT}{F} \log \frac{x}{y_1} = \frac{RT}{F} \log \frac{2x}{-z_1 + \sqrt{4x^2 + z_1^2}}.$$

It is evident that E and E_1 are of opposite sign.

According to the Procter-Wilson theory, the first important action in the mechanism of tanning results from the tendency for E and E_1 to neutralize each other. The initial rate of tanning will, therefore, be measured by the sum of the absolute values of the potential differences, or

$$\frac{RT}{F} \log \frac{4x^2}{(-z + \sqrt{4x^2 + z^2})\ (-z_1 + \sqrt{4x^2 + z_1^2})}.$$

In this expression, z is measured by the absolute value of the electrical charge on the collagen and z_1 that on the tannin particles, while x represents the hydrogen-ion concentration of the tan liquor. For a fixed value of x, an increase in value of either z or z_1 evidently causes an increase in the rate of tanning.

Now, if we introduce a salt, say sodium chloride, and let its concentration in the tan liquor at equilibrium be represented by

$$u = [Na^+] = [Cl'],$$

from the reasoning in Chapter 5, we see that the initial rate of tanning is now determined by the expression

$$\frac{RT}{F} \log \frac{4(x + u)^2}{[-z + \sqrt{4(x + u)^2 + z^2}] \cdot [-z_1 + \sqrt{4(x + u)^2 + z_1^2}]}.$$

It is apparent that an increase in u, provided it does not increase z or z_1, will cause a decrease in rate of tanning. This explains, in part, the retarding effect of salts upon the rate of tanning. If u is increased without limit, the value of the above expression becomes zero.

When the surface film surrounding the tannin particle has joined the solution constituting the jelly phase of the collagen and thus neutralized the potential difference which each had against the external solution, the actual charges on the collagen and tannin are free to neutralize each other, as in the combination of any two oppositely charged ions which tend to form a slightly dissociated salt.

Like the physical chemistry of the proteins, outlined in Chapter 5, this theory is capable of almost indefinite extension by mathematical treatment. Since the quantitative testing of the theory has only just been begun, such extensions may well be left for some future time. It is worthy of note, however, that the theory has proved a valuable guide in the development of tanning processes and no facts observed in tanning practice have yet been shown to be out of harmony with it.

It is interesting to speculate on the probable combining ratio of collagen and pentadigalloyl glucose. Taking the author's value of 750 as the equivalent weight of collagen and assuming that each digalloyl

radical is capable of combining with collagen, we arrive at a combining ratio of 340 parts of tannin to 750 parts of collagen, or 45.3 per 100 parts of collagen. It may be only a coincidence, but this ratio represents the minimum possible for vegetable tanned leather to pass as fully tanned, at least in the author's experience. On the other hand, when skins are allowed to remain in the tan liquors for months, the ratio approaches the value of 90 parts of fixed tannin per 100 of collagen, but the author has never known it to pass this value in practice. Of course it is appreciated that different tannins may have different molecular weights, which would cause some deviation in the ratio to be expected. Any supposition as to the combining proportions of collagen and tannin is admittedly highly speculative in view of our meagre knowledge of the mechanism of tanning, but where so little is known, such speculations are valuable in forming a nucleus from which to build.

The Procter-Wilson theory does not concern itself with the constitutions of the collagen cation and tannin anion, nor does it deal with possible combinations of collagen and tannin where these have electrical charges of the same sign, a condition which rarely, if ever, occurs in tanning practice.

Thomas and Kelly [21] have recently started an investigation to determine the nature of the combination of collagen and tannin at different pH values. Trunkel [22] had previously shown that the water-insoluble compound of gelatin and tannin can be resolved into its components by digesting with ethyl alcohol, provided the digestion is carried out before the precipitate has dried. After drying, the gelatin-tannin compound is unaffected by alcoholic digestion. Thomas and Kelly studied the effect of alcohol upon collagen tanned at different pH values.

Tan liquors were prepared having pH values of 1, 3, 5, 7, and 9. In the study of hemlock bark extract, portions of hide powder containing 1 gram of dry protein were shaken for 24 hours, at room temperature, with 50 cubic centimeters of tan liquor containing 2.7 grams of solid matter of the hemlock extract. The tanned powders were then filtered and washed in Wilson-Kern extractors until the wash water gave no color upon addition of ferric chloride. The wet powders were then transferred to Thorn extractors and extracted with 95-per cent alcohol. In this type of extractor, the material is extracted by the hot vapors as well as by the condensed solvent.

At intervals the alcoholic extracts were transferred to beakers, evaporated to dryness, dried for 4 hours *in vacuo* at 100° C. and weighed. After apparently complete extraction, the tanned powders also were dried *in vacuo* and weighed, the loss of tannin due to the alcohol extraction being calculated by comparison with a control series not treated with alcohol.

[21] The Difference in Kind or Degree of Tannin Fixation as a Function of the Hydrogen-Ion Concentration. A. W. Thomas and M. W. Kelly. *Ind. Eng. Chem.* (1923); (advance copy).

[22] Gelatine and Tannin. H. Trunkel. *Biochem. Z.* 26 (1910), 458.

Table XXXIV shows the results obtained from weighing the residues from the alcoholic extracts and Table XXXV those obtained from the dry weights of the extracted leathers. Apparently alcohol decomposes most easily those leathers which were tanned at pH values lying between 3 and 5, the region in which tanning is usually done in practice. It is also apparent that leathers tanned at pH values greater than 5 are much more resistant to decomposition than those tanned at values less than 5. Table XXXV also shows the effect of extracting previously dried leathers with alcohol; drying evidently brings about a more permanent fixation of the tannin.

TABLE XXXIV.

EXTRACTION BY ALCOHOL OF FIXED TANNIN FROM LEATHERS TANNED WITH HEMLOCK BARK EXTRACT AT DIFFERENT pH VALUES. FIGURES OBTAINED BY WEIGHING THE DRY RESIDUES FROM THE ALCOHOLIC EXTRACTS.

Tanned at pH Value of	Per cent of Total Fixed Tannin Removed by Extraction for 1 hour	45 hours	91 hours
1	6.1	19.3	23.3
3	7.7	24.1	28.9
5	7.8	17.1	22.0
7	3.1	6.9	9.8
9	4.2	6.3	8.4

TABLE XXXV.

(Same Experiment as Described in Table XXXIV. But the figures in this table were obtained by weighing the dry leather after the alcohol extraction.)

Tanned at pH Value of	Per cent of Total Fixed Tannin Removed by 91 Hours' Extraction of the Wet leather	Dried leather
1	16.6	0.0
3	23.3	2.8
5	25.1	4.4
7	4.6	0.6
9	0.6	0.0

A curious finding is that the figures in Table XXXV show a smaller loss of tannin than those in Table XXXIV. Some light is thrown upon this difference by a series of experiments with gambier. These were similar to the hemlock series except for the fact that the 50-cubic centimeter portions of tan liquor contained 2 grams of dry gambier solids. Table XXXVI shows the results obtained by weighing the dry leathers after extraction with alcohol. The leather tanned at a pH value of 9 actually shows a *gain* in weight upon extraction with alcohol. Thomas and Kelly suggest the hypothesis that this gain may be due to an oxidation of the alcohol to aldehyde followed by an aldehyde tannage. Tan liquors absorb oxygen readily at a pH value of 9 and darken in color as oxidation proceeds. The author has found

that oxidized tannins present in leather cause an oxidation of unsaturated oils used in fatliquoring leather, as determined by the ratio of oxidized to unoxidized fatty acids subsequently extracted from the leather. It is therefore not unreasonable to suppose that tannins which have been oxidized at a pH value of 9 may be able to bring about an oxidation of the alcohol molecule.

TABLE XXXVI.

EXTRACTION BY ALCOHOL OF FIXED TANNIN FROM LEATHERS TANNED WITH GAMBIER EXTRACT AT DIFFERENT pH VALUES. FIGURES OBTAINED BY WEIGHING DRY LEATHERS AFTER THE ALCOHOL EXTRACTION.

Tanned at pH Value of	Per cent of Total Fixed Tannin Removed by Extraction for 91 Hours of the Wet Leathers
1	17.5
3	26.3
5	19.5
7	0.7
9	(Gain of 13.8 per cent!)

The most important finding in this work is that the kind of fixation of tannin by collagen at pH values lower than 5 is different from that at pH values greater than 5. The simple theory of Procter and Wilson does not take into consideration the complex organic reactions which apparently occur in tanning with liquors having a pH value greater than 5, nor the changes in the collagen-tannin compound which take place upon drying and aging.

Oxidation Theory.

Of the various theories of tanning treating the subject from the standpoint of organic chemistry, the oxidation theory supported by Meunier, Fahrion, and others is the only one meriting serious consideration. Meunier[23] and his co-workers found that skin could be converted into leather by bringing it into contact with a solution of benzoquinone. The color of the skin changed successively to light rose, to violet, and to brown. A leather of remarkable resistance to boiling water was obtained. An observation of great theoretical significance was that a portion of the quinone was reduced to quinol during the tanning action. Meunier concluded that part of the quinone had been reduced by the oxidation of the collagen and that only the oxidized collagen entered into combination with the remaining quinone. He likened the action to that of quinone upon aromatic amines:

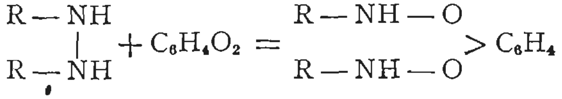
$$C_6H_5NH_2 + 2C_6H_4O_2 = C_6H_5N(C_6H_4O_2) + C_6H_4(OH)_2$$
$$2C_6H_5NH_2 + 3C_6H_4O_2 = (C_6H_5N)_2C_6H_4O_2 + 2C_6H_4(OH)_2 .$$

[23] Modern Theories of the Various Methods of Tanning. L. Meunier. *Chimie & industrie* 1 (1918), 71, 272; English translation, *J. Am. Leather Chem. Assoc.* 13 (1918), 530.

Assuming the existence of primary amino groups in the collagen molecule, the compounds formed might be represented by the formulas:

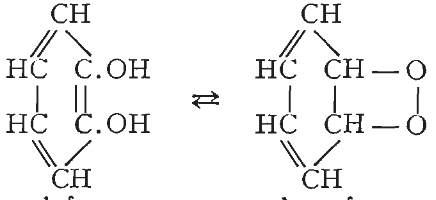
Fahrion[24] suggested the following reactions:

$$2RNH_2 + O = R - NH - NH - R + H_2O$$



In vegetable tanning materials, Meunier assumes that quinones are formed by oxidation and that it is these which react with collagen to form leather.

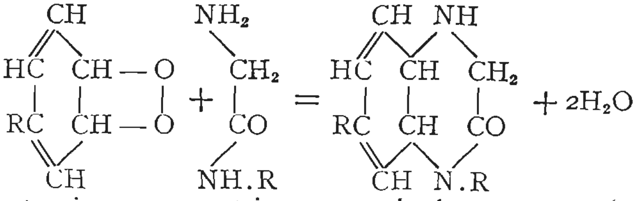
Powarnin[25] objected to the assumption of the formation of quinones by oxidation and suggested that they are formed by a tautomeric change, thus



enol form keto form

The enol form was supposed to be stable chiefly in alkaline solution and the keto form in acid solution.

According to Powarnin's view, only the keto form has tanning properties, the action being represented as follows:



tannin protein leather

The organic chemistry of vegetable tanning has not yet passed the stage of speculative hypotheses.

[24] W. Fahrion. *Mon. sci.* (1911), 361; (1914), 112.

[25] Active Carbonyl and Tannage with Organic Substances. G. Powarnin. *Collegium* (1914), 634.

Chapter 14.

Chrome Tanning.

Although the tanning of skins by means of chromium salts is only of comparatively very recent origin, a large proportion of the world's supply of light leathers is now tanned by this process. In 1858 Knapp[1] described a process for tanning skins with salts of aluminum, iron, and chromium, but chrome tanning did not come into prominence commercially until after the appearance of the patents of Augustus Schultz, of New York, in 1884. In Schultz's process, the skins, after bating or deliming, were tumbled in a solution of potassium bichromate and hydrochloric acid until the chromate had completely penetrated the skins, after which they were allowed to drain. They were then tumbled in a solution of sodium thiosulfate acidified with hydrochloric acid, which reduced the chromate to chromic salt, in which condition it combines with the skin protein, yielding a very stable leather.

Schultz's system of tanning is known as the two-bath process. In 1893 Martin Dennis patented a system for tanning skins directly in a solution of basic chromium chloride along the lines suggested by Knapp in 1858. This one-bath process was naturally to be preferred to the two-bath process and soon gained precedence over it, except in the manufacture of glazed kid leathers, where the two-bath process seemed to yield a leather having more desirable properties. No explanation has yet been forthcoming as to why this should be so, although the author believes that the same results can be obtained by the one-bath process, if the reaction of the liquor is made to equal that of the liquor present in the skins during the second bath of the two-bath process. In the ordinary two-bath process, the acidification of the sodium thiosulfate causes a deposition of sulfur in the leather, which affects its properties, but a similar result can be obtained by the use of sodium thiosulfate in the one-bath process. On the other hand, the precipitation of sulfur in the two-bath process can be avoided by using sodium bisulfite as the reducing agent. Basic chromium sulfate was found to be superior to the chloride for one-bath tanning, as well as cheaper, and is now almost universally used.

Commercial one-bath chrome liquors are usually made from chrome alum or from sodium bichromate. A popular method is that devised

[1] Nature and Essential Character of the Tanning Process and of Leather. F. Knapp. J. G. Cotta Buchhandlung (1858); English translation, *J. Am. Leather Chem. Assoc.* 16 (1921), 658.

by Procter[2] in which acidified sodium bichromate solution is reduced to chromic salt by the addition of a solution of glucose. A great variety of reducing agents have since been suggested or patented for the purpose. A very convenient method, described independently by Balderston[3] and Procter,[4] consists in passing sulfur dioxide gas into a solution of sodium bichromate until the reduction is complete. The equation usually given for the reaction is as follows:

$$Na_2Cr_2O_7 + 3SO_2 + H_2O = Na_2SO_4 + 2CrOHSO_4,$$

but this merely indicates the relative basicity of the final liquor, the end product probably being much more complex than this.

In modern practice, it is customary to pickle the skins from the beamhouse before chrome tanning, as described in Chapter 10. This has the advantage of bringing all skins into a uniform condition. After pickling, the skins are put either into a drum or a paddle vat and tumbled or paddled with chrome liquor until completely tanned, which condition is determined by placing a cutting in boiling water. Any untanned portions are converted into gelatin and this causes the piece of skin to shrivel up and curl. When the skin is completely tanned, it is apparently entirely unaffected by boiling water. The rate of penetration of the chromium salts into the skin, the rate of tanning, and the properties of the resulting leather are markedly influenced by changes in concentration of chromium salt, neutral salt, and hydrogen ion. Conditions are made even more complex by the important effects of time, temperature, and degree of hydrolysis of the chromium salts. All of the variables must be adjusted to suit each other as well as the condition of the skin as it enters the tan liquor and the processes to which it is to be subjected after tanning. Probably no two tanneries operate exactly alike and very few would dare to deviate far from the practice found to give good results under their particular conditions of operation.

Chromium Collagenate.

It now seems fairly well established that acid and basic radicals form definite salts with proteins. There is nothing novel about the assumption that chromium, or other metallic radical, can form with collagen a series of salts that might be called chromium collagenates. Moreover, such an assumption is a convenient one, even though it may be shown later that the compound formed is much more complex than would be indicated by the term chromium collagenate.

If the author's[5] value of 750 be accepted for the equivalent weight of collagen, then the smallest amount of chromic oxide required to

[2] H. R. Procter. *Leather Trades Rev.*, Jan. 12, 1897.
[3] L. Balderston. *Shoe & Leather Rep.*, Oct. 18, 1917.
[4] H. R. Procter. *J. Roy. Soc. Arts.* 66 (1918), 747.
[5] Theories of Leather Chemistry. J. A. Wilson. *J. Am. Leather Chem. Assoc.* 12 (1917), 108.

convert 100 grams of collagen into the chromium salt would be (152 x 100)/(6 x 750), or 3.38 grams. Lamb and Harvey[6] found that chrome leather showing less than 2.8 to 3.0 per cent of chromic oxide, based on the dry leather, was invariably undertanned. Based upon actual collagen, the figure would be about 3.4. That the figure 3.38 has some significance will be made more apparent later. This value assumes that all of the three bonds of the chromium ion have entered into combination with the protein and we should expect such a compound to be extremely stable, which chrome leather undoubtedly is.

The most exhaustive studies yet made of the combination of collagen and chromium at measured concentrations of hydrogen ion, chromic oxide, and neutral salt are those of Thomas and his collaborators, which will be given in some detail.

Hydrolysis of Chromium Salts.

Being a salt of a strong acid and a weak base, chromic sulfate hydrolyzes to a very considerable extent in aqueous solution, yielding free sulfuric acid and a series of basic chromic sulfates. Thomas and Baldwin[7,8] followed the change in degree of hydrolysis of chromic salts, under various conditions, by measuring changes in hydrogen-ion concentration. Studies were made of solutions of C.P. chromic sulfate and chromic chloride and also of a typical commercial chrome liquor, which showed by analysis: Cr_2O_3, 14.3 per cent; Fe_2O_3, 1.9 per cent; Al_2O_3, 0.2 per cent; SO_3, 23.5 per cent; Cl, 0.2 per cent; and basicity corresponding to the formula $Cr(OH)_{1.2}(SO_4)_{0.9}$, the sulfate present in excess of that called for by this formula being present as sodium sulphate.

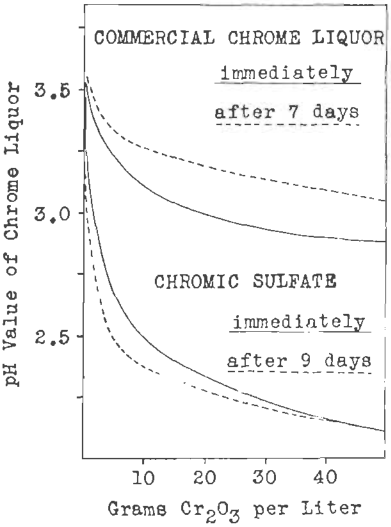


FIG. 127.—Effect of Dilution upon the Hydrolysis of Chrome Liquors.

Effect of dilution: Fig. 127 shows the pH values of both chromic sulfate and the commercial chrome liquor at different concentrations. Strong solutions of each were diluted to increasing extents and the hydrogen-ion measurements were made immediately and also after the diluted solution had stood for 7 or 9 days. With both mate-

[6] Estimation of Chromic Oxide in Chrome Tanned Leather. M. C. Lamb and A. Harvey. *Collegium* (London Edition) (1916), 201.

[7] The Acidity of Chrome Liquors. A. W. Thomas and M. E. Baldwin. *J. Am. Leather Chem. Assoc.* 13 (1918), 192.

[8] Contrasting Effects of Chlorides and Sulfates on the Hydrogen-Ion Concentration of Acid Solutions. *J. Am. Chem. Soc.* 41 (1919), 1981.

rials, the effect of dilution is naturally to raise the pH value, but, upon standing, the pH value of the commercial liquor continues to rise, while that of the chromic sulfate falls.

Effect of added acid or alkali: Fig. 128 shows the effect of adding sulfuric acid or sodium hydroxide to solutions of the commercial chrome liquor and of pure chromic sulfate. In each case a given amount of concentrated chrome liquor was mixed with a definite volume of standard sulfuric acid or sodium hydroxide and the mixture was diluted to 50 cubic centimeters. The hydrogen-ion concentration was determined immediately after mixing and diluting and also after definite intervals of time. The addition of acid causes a corresponding increase in hydrogen-ion concentration, but this causes a repression of hydrolysis of the chromium salt. The curves show that changes in degree of hydrolysis require a considerable length of time; after the addition of acid, the hydrogen-ion concentration continues to fall for many days, approaching, but never reaching the value it had before the addition of the acid.

The lowering of the hydrogen-ion concentration by the addition of alkali causes an increase in the degree of hydrolysis of the chromium salt and the hydrogen-ion concentration continues to rise towards the value it had before adding the alkali. The long time required for such systems to reach equilibrium, after a disturbance, increases the difficulty of investigations of the chemistry of chrome tanning.

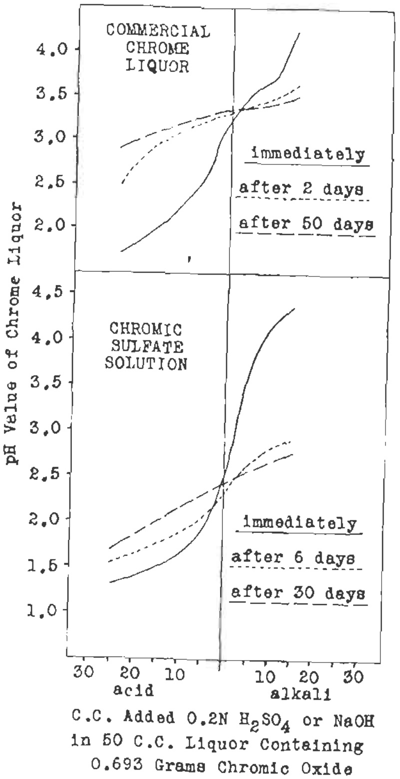


FIG. 128.—Effect of Added Acid or Alkali upon the Hydrolysis of Chrome Liquors.

Effect of neutral salts: In Chapter 4 it was pointed out that the hydrogen-ion concentration of acid solutions is increased by the addition of neutral chlorides and decreased by the addition of neutral sulfates. The effect of increasing concentration of different salts in solutions of sulfuric and hydrochloric acids was shown in Figs. 39 and 40. In Fig. 129 are shown the changes in hydrogen-ion concentration occurring when various salts are added to solutions of the commercial chrome liquor and of pure chromic sulfate. The curves are strikingly similar to those in Figs. 39 and 40. The time effect is shown in the case of sodium chloride; the other measurements were made 30 days

after adding the salt in order to give time for the re-establishment of equilibrium.

In order to avoid the complications obtained by mixing chlorides with chromic sulfate, Thomas and Baldwin also studied the effect of neutral chlorides upon a solution of pure chromic chloride. Fig. 130 shows the effect of adding increasing amounts of various neutral salts

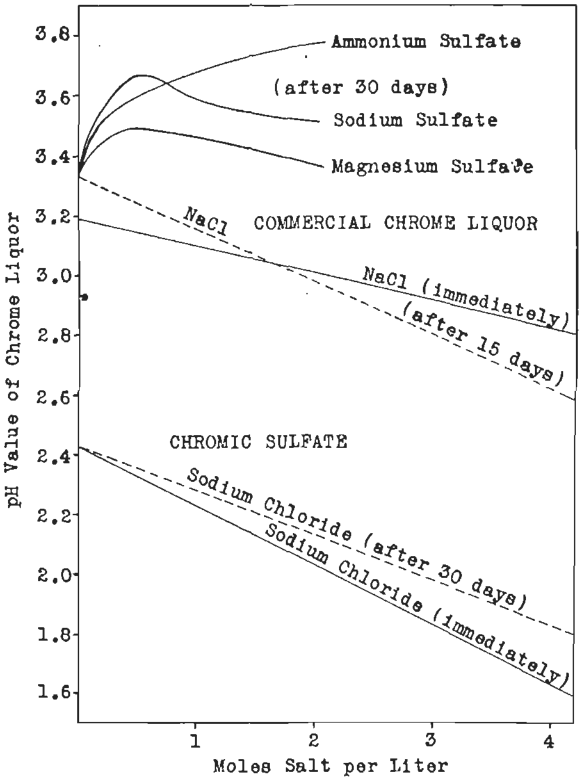


FIG. 129.—Effect of Neutral Salts on the Hydrogen-Ion Concentration of Chrome Liquors Containing 13.86 Grams of Chromic Oxide per Liter.

to a solution of the green modification of chromium chloride; measurements of hydrogen-ion concentration were made immediately after adding the salt and diluting to definite concentration and also after the solutions had stood for 50 days. Where no salt was added, there was a rise in pH value upon standing.

The complex nature of the time effect after adding salt to a chrome liquor is shown in Fig. 131. Commercial chrome liquor and sodium chloride were mixed and diluted so that the final concentration of sodium chloride was twice molar and of chromic oxide 13.86 grams per liter. Determinations of hydrogen-ion concentration were made every

10 minutes for 4 hours and then at longer intervals for 3 days. It is evident that the action causing the increase in hydrogen-ion concentra-

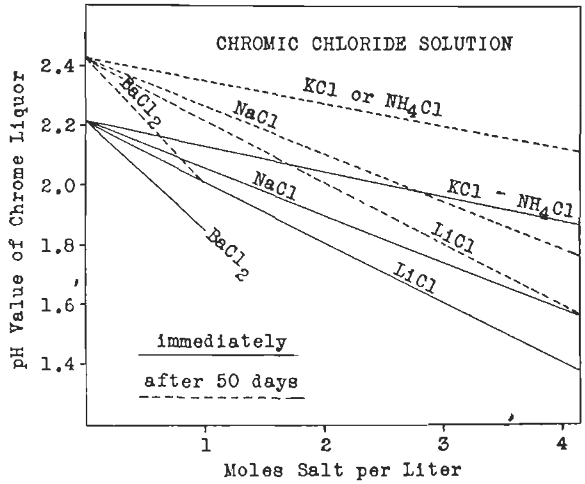


FIG. 130.—Effect of Neutral Chlorides on the Hydrogen-Ion Concentration of a Solution of Chromic Chloride Containing 13.77 Grams of Chromic Oxide per Liter.

tion is subject to a time factor as well as the hydrolysis of the chromium salt.

Following the observation by W. Klaber that chrome liquors can be made more basic, without causing precipitation, if salt be added to

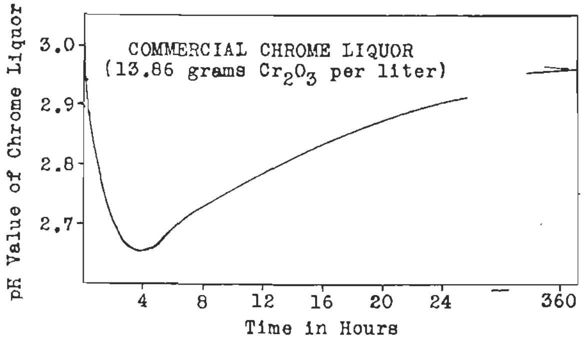


FIG. 131.—Change in Hydrogen-Ion Concentration of Chrome Liquor with Time after the Addition of 2 Moles of Sodium Chloride per Liter.

them previously Wilson and Kern[9] noted that the resistance of a chrome liquor to precipitation by alkali is increased by the addition of

[9] The Action of Neutral Salts upon Chrome Liquors. J. A. Wilson and E. J. Kern J. Am. Leather Chem. Assoc. 12 (1917), 445.

all neutral salts and that sulfates are even more effective than chlorides. The amount of alkali required to start precipitation in a chrome liquor was determined by titrating 10 cubic centimeters of filtered liquor with 0.1N sodium hydroxide until the first permanent turbidity appeared, as seen by looking through the liquor. For a given chrome liquor, 3.7 cubic centimeters of standard alkali were required. To another portion of 10 cubic centimeters was added 0.04 gram molecule of sodium chloride; in this case 6.8 cubic centimeters of the standard alkali were required to start precipitation. Repeating the experiment, taking in each case 10 cubic centimeters of the chrome liquor and 0.02 gram molecule of added salt, the following amounts of standard alkali were required to start precipitation in the presence of the neutral salt indicated: none, 3.7; KBr, 3.9; KCl, 4.0; KNO_3, 4.2; NH_4Cl, 4.5; $NaCl$, 5.4; $MgCl_2$, 6.2; $MgSO_4$, 10.5; Na_2SO_4, 11.4; and $(NH_4)_2SO_4$, 11.6. At least some of the effect of the chlorides may be attributed to their action in increasing the hydrogen-ion concentration of the liquor. The sulfates, however, decrease the hydrogen-ion concentration, but, since they increase the stability of the chrome liquor, it seems likely that they form addition compounds with the chromium salt less easily precipitated than the simpler salt.

Diffusion of Chromium Salts into Protein Jellies.

In vegetable tanning, the rate of diffusion of tannin into the fibers of the skin increases with increasing pH value. In chrome tanning, the reverse is true. An increasing pH value causes the molecules of chromium salt to form aggregates of increasing size, greatly reducing the rate at which they diffuse into the skin.

When neutral skin substance is brought into contact with a chrome liquor, both the free acid present in the liquor and the basic chromic salt begin to diffuse into it. But the greater rate of diffusion of the acid causes the liquor to become more basic. Procter and Law[10] studied the relative rates of diffusion of the free acid and chromium salt of a chrome liquor into gelatin jelly by allowing a faintly alkaline solution of gelatin and phenolphthalein to set in a Nessler tube and pouring the chrome liquor on top of the jelly. As the acid diffuses into the jelly, it discharges the color of the phenolphthalein, while the extent of diffusion of the chromium salt can be followed by its color. The combination of both acid and chromium with the gelatin has a retarding effect upon the rate of diffusion.

This differential diffusion may not occur where the common practice of pickling skins prior to tanning is used. When the skins contain a great excess of acid, the chromium salt diffuses into them very rapidly, but the rate of combination of chromium and collagen is correspondingly decreased and it becomes necessary to neutralize some of the acid before the skins can become completely tanned, even though completely permeated by the chromium salt.

[10] H. R. Procter and D. J. Law. *J. Soc. Chem. Ind.* 28 (1909), 297.

The Time Factor in Chrome Tanning.

The progress of the chrome tanning of hide powder with time has been studied by Thomas, Baldwin, and Kelly.[11 12] They first examined the action of the commercial chrome liquor described above. The chrome liquor was diluted to contain 17 grams of chromic oxide per liter. Two hundred-cubic centimeter portions were poured upon 5-gram portions of hide powder in glass-stoppered bottles. These mixtures were kept at room temperature (about 26° C.), agitated frequently, and filtered off at definite intervals,—1, 2, 4, 6, 8, 12, 24, 48, 72, and 96 hours. They were filtered by suction on a dry paper in a Buchner funnel, the filtrate was set aside for analysis, and the tanned powder was washed with 500 cubic centimeters of water in order to remove chromium salts

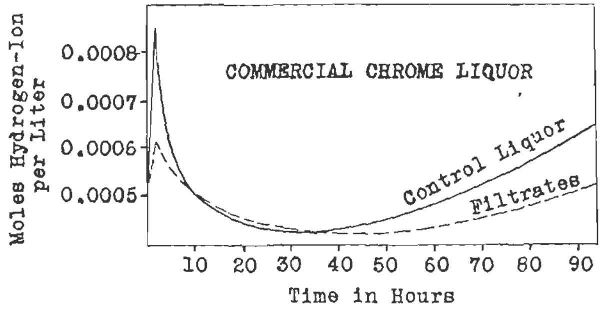


FIG. 132.—Change in Hydrogen-Ion Concentration of Chrome Liquors with Time.

not chemically combined. The washed powder was partially dried at 40° C. and then completely at 100° C.

The filtered liquors were analyzed for hydrogen ion, acidity, and chromic oxide and the tanned powders for sulfate, chromic oxide, ash, and hide substance (nitrogen x 5.62).

Measurements of hydrogen-ion concentration were made immediately upon filtration of the liquors and, in order to exclude the possibility of attributing natural hydrolytic changes to absorption by hide substance, parallel measurements were made upon a portion of the chrome liquor having no contact with hide powder. The parallel sets of measurements are shown in Fig. 132.

In Fig. 133 are shown the amounts of chromic oxide and of sulfate combined with 1 gram of skin protein at different intervals of time. These were obtained from the analyses of the washed powders after tanning. The broken lines represent calculations made from analyses of the chrome liquors on the assumption that the concentration is uni-

[11] The Time Factor in the Adsorption of the Constituents of Chrome Liquor by Hide Substance. A. W. Thomas, M. E. Baldwin, and M. W. Kelly. *J. Am. Leather Chem. Assoc.* 15 (1920), 147.

[12] The Time Factor in the Adsorption of Chromic Sulfate by Hide Substance. A. W. Thomas and M. W. Kelly. *Ibid.*, 15 (1920), 487.

form throughout all of the solution present in the system during tanning. We know from Chapter 5 that this assumption is not true, that the solution absorbed by the collagen jelly is less concentrated than the outer solution. This explains why these curves show lower values for combined sulfate and chromic oxide. Thomas and Kelly were well aware of this fact and presented the calculations made from the analysis of the solutions for the purpose of demonstrating the fallacies in this

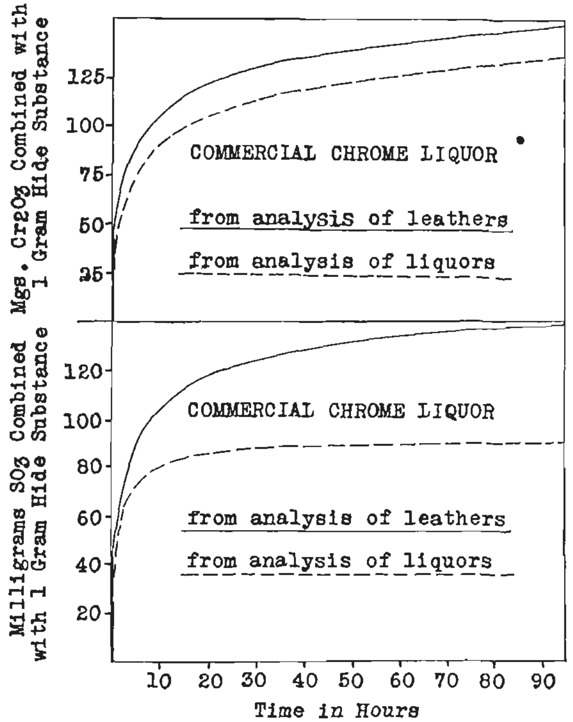


FIG. 133.—Progress of Combination of Cr_2O_3 and SO_3 with Hide Substance during 4 Days' Contact with Chrome Liquor containing 17 Grams Cr_2O_3 per Liter.

method, which is commonly used for measuring the extent of "adsorption" of substances from solution by skin and other materials. The discrepancy is increased in the case of the sulfate determination by the fact that some combined sulfate is removed by washing, whereas the chromium-collagen compound is very stable.

They next studied the action of a solution of pure chromic sulfate, but, using the same procedure, got only erratic results. They found it necessary, when using the pure salt, to soak the hide powder in water before adding the chrome liquor. The fact that the pure salt gave a solution very much more acid than the commercial salt may have had something to do with this. Five-gram portions of hide powder were

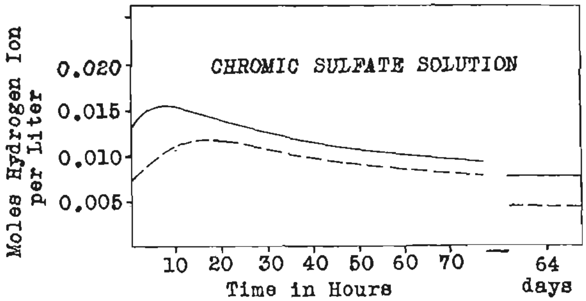


FIG. 134.—Change in Hydrogen-Ion Concentration of Chrome Liquors with Time.

placed in each of a series of glass-stoppered bottles, 50 cubic centimeters of water were added to each, and the powders were allowed to soak over night. Then 150 cubic centimeters of chromic sulfate solution were

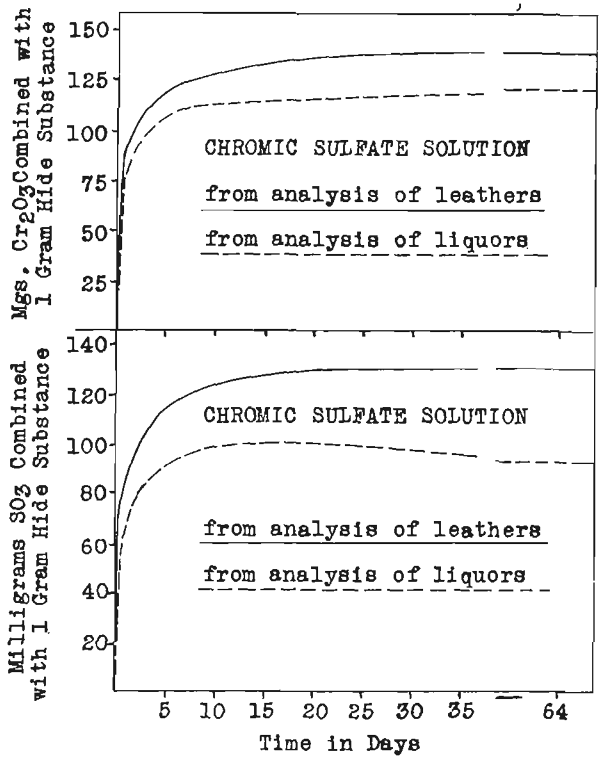


FIG. 135.—Progress of Combination of Cr_2O_3 and SO_3 with Hide Substance during 64 Days' Contact with Chromic Sulfate Solution containing 16.4 Grams Cr_2O_3 per Liter.

added, making 200 cubic centimeters of liquor with a concentration of 16.4 grams of chromic oxide per liter. The rest of the experiment was performed just as in the case of the commercial chrome liquor, except for the fact that a time period of 64 days was covered.

The variation in hydrogen-ion concentration in the control liquor and in the filtrates from the tanning tests is shown in Fig. 134. The trend of the curves is different from that of those in Fig. 132.

The amounts of chromic oxide and of sulfate combined with 1 gram of hide substance are shown in Fig. 135. When the calculations were made from the analyses of both leathers and liquors, the same sort of differences were noted as with the commercial chrome liquor. The only reliable figures are those obtained from the analyses of the leathers, shown by the continuous lines. The amount of chromic oxide combined with 100 grams of hide substance approaches a limiting value of 13.8 grams. Because this is almost exactly 4 times the author's value of 3.38 grams, calculated to be the smallest amount of chromic oxide required to convert 100 grams of collagen into the chromium salt, Thomas and Kelly referred to it as tetrachrome leather.

A comparison of Figs. 133 and 135 will show that the rate of tanning is very much less in the chromic sulfate solution, in which the hydrogen-ion concentration is about 20 times as great as in the commercial liquor. It will also be noted that the amount of chromic oxide combined with 1 gram of skin protein is greater for the commercial liquor after 4 days than the limiting value in the case of the pure chromic sulfate and has not reached a limiting value in 4 days. The significance of this will be made more apparent presently.

The Concentration Factor in Chrome Tanning.

The effect of the concentration of a chrome liquor upon the fixation of chromium by skin protein has been studied by Baldwin [13] and by Thomas and Kelly.[14, 15] A solution of the commercial chrome liquor, described above, was made having a concentration of 202 grams of chromic oxide per liter and this was used at various dilutions to study the effect of concentration. A 200-cubic centimeter portion of each dilution was poured into a bottle containing hide powder equivalent to 5 grams of water-free hide powder. Another portion of each solution was set aside and at the expiration of 48 hours the hydrogen-ion concentration was determined. The bottles were shaken at intervals for 48 hours and the contents were then filtered off by suction. Analyses were made of the liquors and of the tanned powders after washing and drying, the methods employed being the same as in the studies of the time factor.

[13] The Effect of the Concentration of a Chrome Liquor upon Adsorption by Hide Substance. M. E. Baldwin. *J. Am. Leather Chem. Assoc.* 14 (1919), 433.

[14] The Effect of Concentration of Chrome Liquor upon the Adsorption of Its Constituents by Hide Substance. A. W. Thomas and M. W. Kelly. *J. Ind. Eng. Chem.* 13 (1921), 31.

[15] Equilibria between Tetrachrome Collagen and Chrome Liquors; the Formation of Octachrome Collagen. *Ibid.*, 14 (1922), 621.

Fig. 136 shows the variation in hydrogen-ion concentration in the filtrates and also in the control liquors which had no contact with hide powder. Fig. 137 shows the effect of concentration upon the amount of chromic oxide fixed by 1 gram of skin protein in 48 hours. Where the calculation was made from the analyses of the liquors, a ridiculous result was obtained, as expected. In this calculation it is assumed that the decrease in concentration of the liquor represents the amount of solute combined with the hide powder, but the concentration of the stronger liquors is actually increased by the introduction of hide powder,

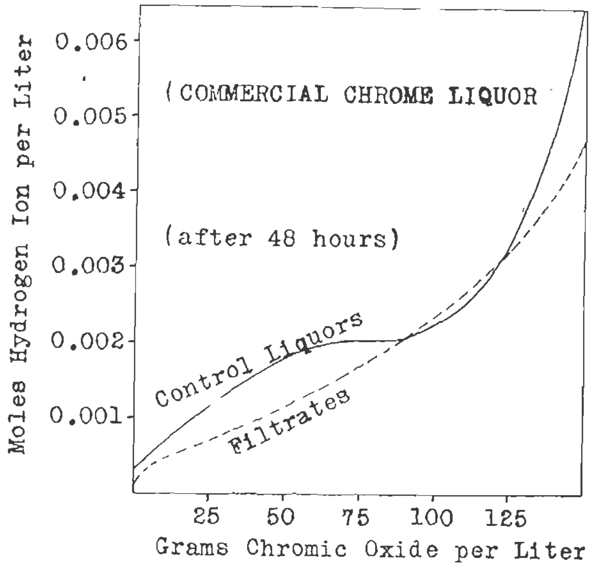


FIG. 136.—Change in Hydrogen-Ion Concentration of Chrome Liquors with Increasing Concentration.

due to the absorption of a greater proportion of water to chromium salt than existed in the solution before the introduction of the hide powder. It is interesting to note that the method of calculation giving these ridiculous results is the same in principle as that of the official method of tannin analysis of the American Leather Chemists Association, described in Chapter 12. The determination of combined chromium by analysis of the washed leathers corresponds to the Wilson-Kern method of tannin analysis, also described in Chapter 12.

The reason for the point of maximum at a concentration of 15 grams of chromic oxide per liter is not entirely clear, although a number of causes may be assigned to the falling off in rate of combination at higher concentrations, among which may be mentioned the increasing hydrogen-ion concentration, as shown in Fig. 136, the increasing salt concentration, and the probability of the formation of addition compounds. It is interesting to compare this curve with those for the rate

of vegetable tanning as a function of concentration, shown in Chapter 13.

The experiments just described were repeated exactly, except for the fact that the hide powders were kept in the chrome liquors for 8.5 months. The results are shown in Fig. 138. Curiously enough a point of maximum occurs having a value of 26.6 grams of chromic oxide per 100 grams of skin protein, which is approximately 8 times the author's calculated minimum of 3.38. Moreover a point of inflection occurs in the curve at a point giving just half of the maximum value. On the

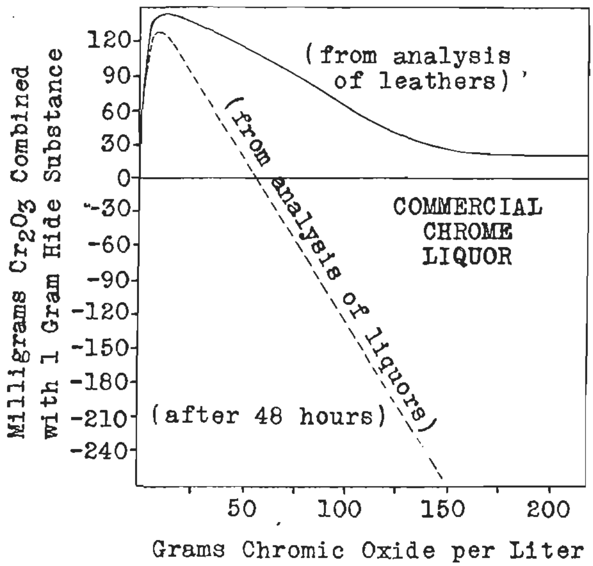


FIG. 137.—Effect of Concentration of Chrome Liquor upon Combination of Chromium with Hide Substance.

assumption that they had obtained octachrome collagen, Thomas and Kelly calculated the combining weight of collagen as 94, a value of the same order of magnitude as those of the amino acids making up the protein molecule. This degree of combination of collagen and chromium is the highest ever reported in the literature.

The fact that only a tetrachrome collagen was obtained after 64 days of contact with chromic sulfate solution, whereas an octachrome collagen was obtained with the commercial chrome liquor may possibly be explained by the differences in hydrogen-ion concentration of the two series of liquors. On this assumption, only half of the total number of carboxyl groups are capable of attaching chromium bonds at the higher acidities. The possibility is thus suggested that a series of collagen salts from monochrome to octachrome might be obtained by tanning hide powders for a sufficient length of time at different pH

values. Experiments to settle this point will be made as soon as the opportunity affords.

The reversibility of the action leading to the formation of tetrachrome collagen was studied by Thomas and Kelly. Since the chrome

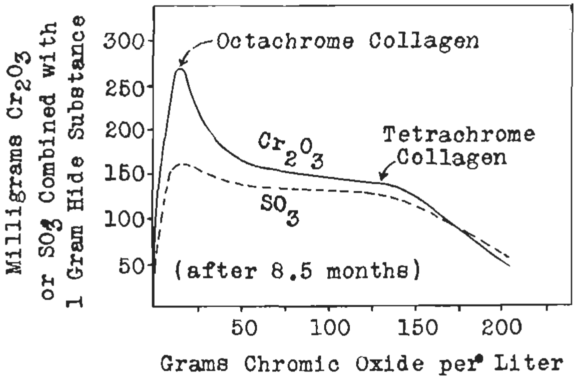


FIG. 138.—Effect of Concentration of Chrome Liquor upon Combination of Chromium and Sulfate with Hide Substance.

tanned hide powder does not lose any measurable amount of chromium upon several hours' washing, they decided to allow tetrachrome collagen to remain in contact with solutions of varying chromium content for several months.

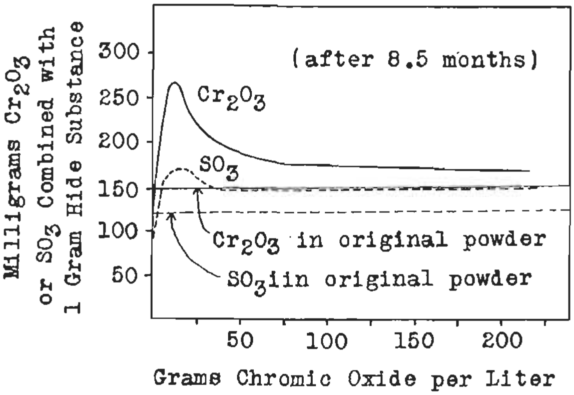


FIG. 139.—Effect of Concentration of Chrome Liquor upon Combination of Chromium and Sulfate with Tetrachrome Collagen.

Portions of tetrachrome collagen containing just 5 grams of hide substance were placed in a series of 12 bottles and covered with 200-cubic centimeter portions of chrome liquor of various concentrations. The bottles were kept sealed to prevent evaporation and were shaken once a week. At the end of 8.5 months the contents were filtered and

the powders washed free from soluble matter, dried, and analyzed. The results are shown in Fig. 139. They show that a hydrolysis of the chrome collagen and collagen sulfate compounds takes place in water and in very dilute chrome liquor, which was also shown by an increase in hydrogen-ion concentration.

With further increase in concentration of the chrome liquor, there is a steady addition of Cr_2O_3 and SO_3, approaching the condition of octachrome collagen. But with further increase in concentration the

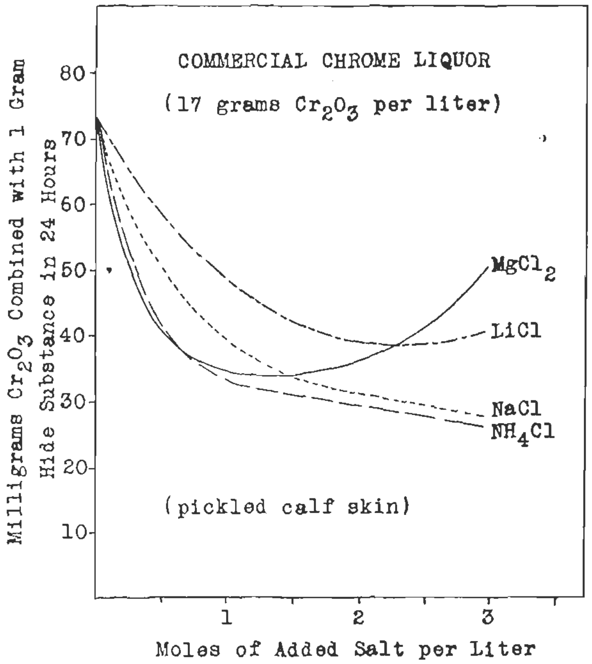


FIG. 140.—Retardation of Chrome Tanning by Neutral Salts at Various Concentrations.

curve does not fall below the tetrachrome value. This shows that the curve in Fig. 138 does not represent the equilibrium condition of a reversible reaction. On the contrary, it suggests that the fall in the curves is due to the increasing hydrogen-ion concentration, which inhibits the combination of collagen and chromium.

Effect of Neutral Salts upon Chrome Tanning.

In studying the effect of neutral salts upon the chrome tanning of calf skin, Wilson and Gallun [16] selected sodium sulfate and the chlorides of ammonium, sodium, lithium, and magnesium because of their different degrees of hydration in aqueous solution. The commercial chrome

[16] The Retardation of Chrome Tanning by Neutral Salts. J. A. Wilson and E. A. Gallun. *J. Am. Leather Chem. Assoc.* 15 (1920), 273.

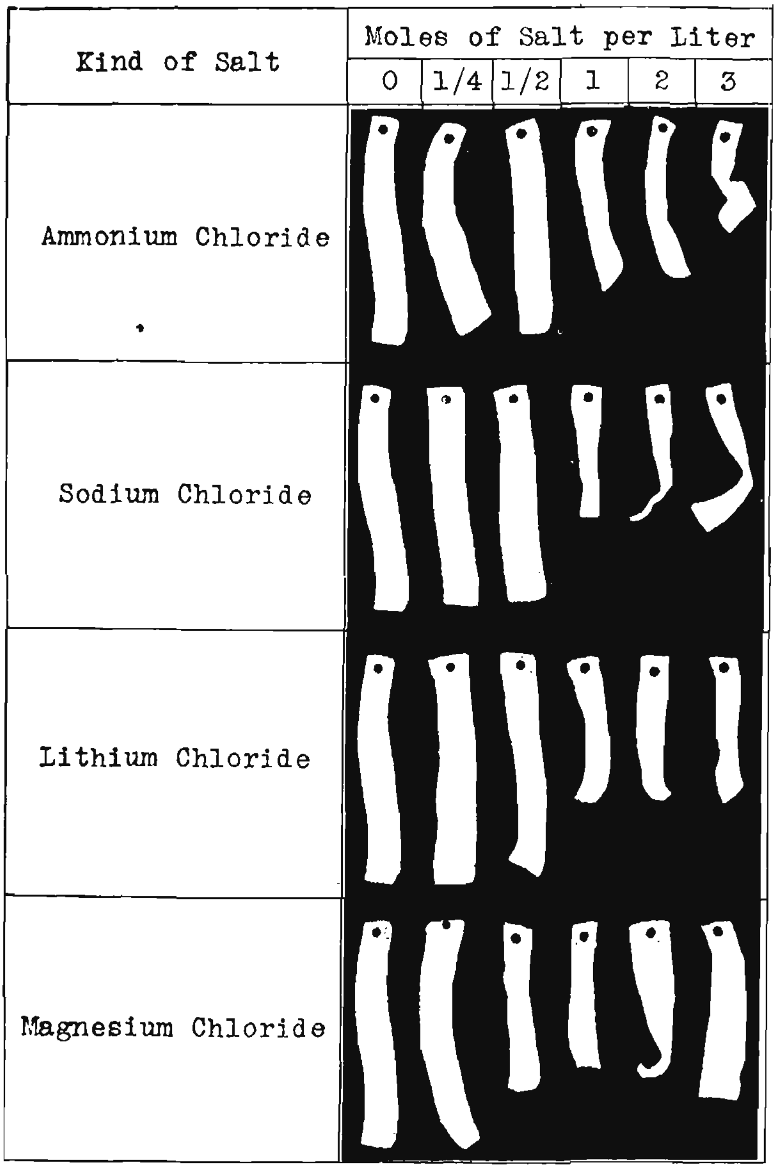


Fig. 141.—Strips of Chrome Leather, All Originally of Equal Area, Taken After Tanning for 24 Hours and Then Boiling in Water for 5 Minutes and Drying. Compare with Curves in Fig. 140.

mixture which they used showed by analysis: Cr_2O_3, 24.2 per cent; Fe_2O_3, 0.6 per cent; Al_2O_3, 2.7 per cent; SO_3, 39.5 per cent; Cl, 0.4 per cent; and basicity corresponding to the formula $Cr(OH)_{1.4}(SO_4)_{0.8}$. Solutions of this chromium preparation were mixed with solutions of the various neutral salts so as to give liquors containing 17 grams of chromic oxide per liter and definite quantities of salt.

In each test a strip of pickled calf skin, 16 square inches in area, was covered with 200 cubic centimeters of chrome liquor, in a bottle, and shaken at intervals for 24 hours. The pieces of skin were then washed by shaking with successive changes of water until the wash water gave only a very faint test for chloride or sulfate. Strips of equal area were cut from each piece and immersed in boiling water for 5 minutes, in order to determine the nearness to complete tannage. The remaining portions were cut into small pieces, dried and analyzed. The effect of increasing concentration of the chlorides of ammonium, sodium, lithium, and magnesium upon the amount of chromic oxide combined with a unit of hide substance in 24 hours is shown in Fig. 140. In Fig. 141 are shown the strips of skins after being subjected to the action of boiling water for 5 minutes. The appearance of these strips parallels the curves, in a rough sort of way; that is, they generally show the greatest shrinkage in area where the amount of combined chromic oxide is smallest. The first strip in each series proved to be fully tanned and showed no shrinkage in area.

In another series of tests, chrome liquor having a concentration of 10 grams of chromic oxide per liter was used and the effect of sodium sulfate was studied in addition to the effect of the chlorides noted above. The results for the chlorides were practically the same as in the first experiment, except for the observation of a point of minimum in the sodium chloride curve at 2 moles per liter of salt and a slight rise to 3 moles. In the case of the sodium sulfate, there was a steady drop in fixation of chromic oxide from 10.09 grams per 100 of hide substance when no added salt was present to 3.57 when the solution was saturated with the salt.

Wilson and Gallun attributed the action of the chlorides, in part, to their hydration. The removal of water from the rôle of solvent would have the practical effect of increasing the concentration of all of the constituents of the chrome liquor, expressed in terms of the free solvent. Fig. 137 shows that increasing the concentration of the chrome liquor from 17 grams of chromic oxide per liter does retard the rate of combination of collagen and chromium. That the chlorides actually concentrate the solute in the free solvent is also indicated by the fact that they increase the hydrogen-ion concentration as measured by the hydrogen electrode. But at half-molar concentration the effect only of magnesium chloride is in its expected relative position; being most highly hydrated it should produce the greatest effect, which it does. At 3-molar concentration all 4 chlorides are in an order inverse to that expected unless it may be assumed that at very high concentrations of chrome liquor a further increase in concentration causes an increased rate of tanning.

The action of sulfates is in a category different from that of the chlorides, as shown by the fact that they decrease the hydrogen-ion concentration of acid solutions and of chrome liquors. Wilson and Gallun suggested that the retarding action of sodium sulfate was probably due to the formation of addition compounds between the added salt and the chromium compounds which tan less readily than the original chromium compounds, but that the action was further complicated by the hydration of the sodium sulfate.

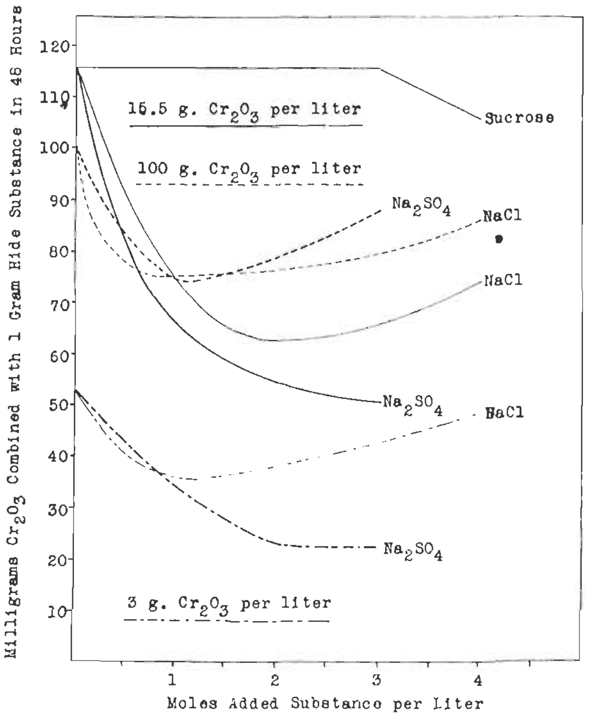


FIG. 142.—Retardation of Chrome Tanning by Neutral Salts and by Sucrose at Various Concentrations.

In the hope of throwing further light on this complex action, Thomas and Foster [17] studied the actions of sodium chloride, sodium sulfate, and sucrose upon chrome tanning. They prepared a pure chrome liquor by reducing pure sodium bichromate with sulfur dioxide and then expelling the excess of this gas. Portions of hide powder equal to 5 grams of hide substance were covered with 50 cubic centimeters of

[17] Influence of Sodium Chloride, Sodium Sulfate and Sucrose on the Combination of Chromic Ion with Hide Substance. A. W. Thomas and S. B. Foster. *J. Ind. Eng. Chem.* 14 (1922), 132.

water in bottles and allowed to stand over night, when the salt or sugar to give the desired concentration was added. Finally 150 cubic centimeters of chrome liquor were added, of such concentration that if it were diluted to 200 cubic centimeters it would contain 3, 15.5, or 100 grams of chromic oxide per liter. The mixtures were rotated in a tumbling machine for 48 hours, filtered through muslin bags, and washed well with tap water and 3 times with 200-cubic centimeter portions of distilled water. The washed powders were then dried and analyzed as usual.

The effect of increasing concentration of sodium sulfate, sodium chloride, and of sucrose is shown in Fig. 142. Analysis of the filtrates from the series of chrome liquors of intermediate concentration showed that increasing concentration of sodium chloride lowered the pH value from 2.90 to 2.20, while sodium sulfate raised it to 3.01. This contrasting effect is similar to that shown in Fig. 129.

The curves representing the effect of sodium chloride all have points of minimum followed by an upward trend, which, in the case of sodium sulfate, is shown only where the chrome liquor is very concentrated. But sucrose is evidently without effect, except at 4-molar concentration.

Because sucrose, which is hydrated in aqueous solution, shows no retarding effect upon chrome tanning up to 3-molar concentration, Thomas and Foster concluded that the retarding effect of the salts is probably due to some cause other than their hydration. They suggested that chlorides, as well as sulfates, form addition compounds with chromium salts rendering them less dissociated and, consequently, less active in combining with the skin protein. They liken the action to the decrease in toxicity of mercuric chloride in the presence of sodium chloride, which Rona and Michaelis[18] ascribe to the formation of the complex ions $HgCl_3'$ and $HgCl_4''$. Upon increasing the concentration of salt still further, the hydration effects a virtual concentration of the chromium ions to such an extent that the retarding action of the addition compound formation is counterbalanced by the activity of the high concentration of chromium ion and the curves begin to slope upward.

It may be questioned as to whether we are safe in drawing conclusions regarding the effect of hydration from the experiments with sucrose. Corran and Lewis[19] found that potassium and chloride ions are soluble in the water of hydration of sucrose. The effect of neutral salts upon the hydrogen-ion activities of acid solutions, described in Chapter 4, seem to indicate that ions are not soluble in the water of hydration of salts. Thomas and Foster ascribe the retardation of chrome tanning by 4-molar sucrose to the formation of a compound with chromium, analogous to the combination with other hydroxy compounds, such as tartrates. As will be shown presently, such compounds of chromium have no tanning power.

[18] *Biochem. Z.* 97 (1919), 85.
[19] The Effect of Sucrose on the Activities of the Chloride and Hydrogen Ions. J. W. Corran and W. C. M. Lewis. *J. Am. Chem. Soc.* 44 (1922), 1673.

Effect of Salts of Hydroxy-Acids upon Chrome Tanning.

While investigating the failure of certain types of chrome liquor to tan pickled calf skin, Procter and Wilson [20] found that the tanning action is checked and may even be reversed by the introduction of salts of hydroxy-acids into the chrome liquor.

After the addition of Rochelle salt (potassium sodium tartrate) to a chrome liquor, a change occurs in the liquor which requires a considerable length of time for completion. Immediately after the addition, the chrome liquor is still precipitable by alkali, but the precipitate slowly redissolves with time. If the liquor is allowed to stand for several hours before the addition of alkali, no precipitate forms at all. A color change in the liquor is also noticeable.

A chrome liquor was made by rendering a solution of chrome alum basic with sodium carbonate and from this a series of solutions was prepared having a concentration of 13 grams of chromic oxide per liter and Rochelle salt in concentration ranging from zero to 50 grams per liter. A piece of calf skin was put into each solution, which was agitated occasionally for 24 hours. At the end of this time, all pieces in solutions containing 10 grams per liter or less of Rochelle salt were completely tanned, as determined by the boiling test, but those in the stronger solutions were not. These solutions all gave precipitates upon addition of sodium carbonate; that containing 25 grams of the salt per liter gave a slight precipitate and that containing 50 grams gave none. The piece in the solution containing 25 grams became tanned after the addition of sodium carbonate but that in the solution containing 50 grams could not be made to tan, regardless of the amount of alkali added. That the action of the Rochelle salt was on the chromium salts and not on the skin was proved by washing the skin that was still not tanned and placing it in a liquor containing no Rochelle salt, in which it quickly became fully tanned.

The same results were obtained when the experiment was repeated with sodium citrate. The sodium salts of lactic, gallic, and salicylic acids were also found to prevent the precipitation of chrome liquor by alkali. Procter and Wilson attributed the action of Rochelle salt to the formation of a complex chromi-tartrate ion analogous to the cupri-tartrate ion of Fehling's solution.

The fact that Rochelle salt will dissolve precipitates of chromic hydroxide led Procter and Wilson to suspect that it might have the power to decompose chrome leather. They soaked a piece of fully tanned leather in a normal solution of Rochelle salt over night and found, next day, that it would not stand the boiling test. But after washing and soaking in fresh chrome liquor, containing no Rochelle salt, it soon became fully tanned again. It was found that chrome leather can be detannized by Rochelle salt solution and then tanned again in fresh chrome liquor repeatedly, showing that chrome tanning is a reversible action, under certain conditions.

[20] The Action of Salts of Hydroxy-Acids upon Chrome Tanning. H. R. Procter and J. A. Wilson. *J. Soc. Chem. Ind.* 35 (1916), 156.

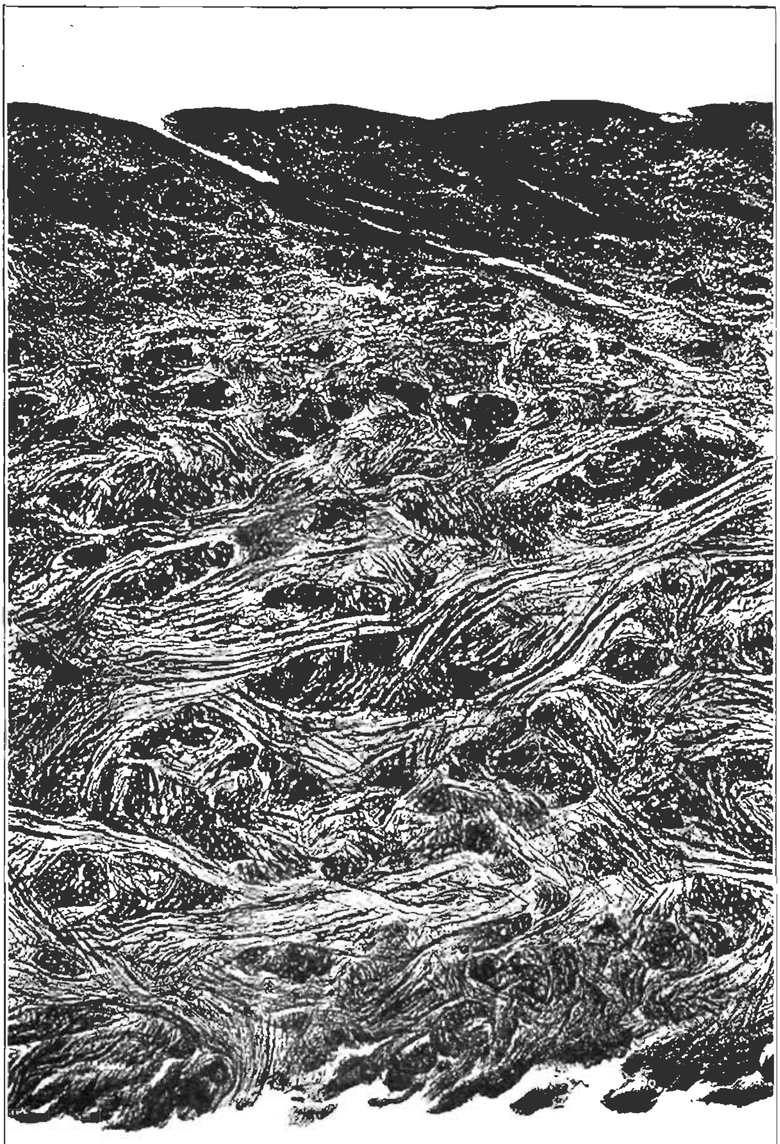


Fig. 143.—Vertical Section of Calf Leather.
(Vegetable tanned.)

Location: butt.
Thickness of section: 40 μ.
Stain: none.
Tannage: vegetable.

Eyepiece: none.
Objective: 16-mm.
Wratten filter: K3-yellow.
Magnification: 80 diameters.

Fig. 144.—Vertical Section of Calf Leather.
(Chrome tanned.)

Location: butt.
Thickness of section: 40 μ.
Stain: none.
Tannage: chrome.

Eyepiece: none.
Objective: 16-mm.
Wratten filter: K3-yellow.
Magnification: 80 diameters.

The extent to which chrome leather can be freed from chromium by Rochelle salt was shown by soaking a piece of chrome leather in a normal solution of Rochelle salt for two weeks. The solution was colored a deep green and the skin, after thorough washing, was found to be practically free from chromium and resembled a piece of bated skin. Upon heating with pure water, it was gradually converted into gelatin and the solution set to a firm jelly upon cooling. This work has since found application in preparing chrome leather wastes for manufacture into glue and for the stripping of the chrome from the surface of leather to be retanned with vegetable tanning materials.

Comparison of Chrome and Vegetable Tanned Leathers.

Ever since chrome tanning was first introduced, the relative merits of chrome and vegetable tanned leathers have formed the subject-matter for debate. Too often, however, the attempt was made to compare a poor grade of one kind of leather with a good grade of the other, without taking into consideration differences in the original skins and in the methods of manufacture of the leathers. Since the resistance of a leather to tearing, for example, is a function of the grease content, the moisture content, and the extent to which the thickness of the original skin has been reduced by splitting, any comparison between two kinds of leather must take all of these factors into consideration. There are, however, certain differences between chrome and vegetable tanned leathers that are incontrovertible and more or less independent of the details of manufacture. These only will be considered in making the comparison.

Figs. 143 and 144 represent vertical sections of vegetable and chrome tanned leathers made from the same skin. After bating, the skin was cut into halves along the line of the back bone. One half was tanned with chrome liquor and the other with vegetable tanning materials. When finished, each leather represented an excellent specimen of shoe upper leather of its particular kind. The sections shown in the figures are from the finished leathers and were cut from exactly corresponding points on the skin.

The outstanding difference in appearance is the much larger size of the fibers of the vegetable tanned leather. In the chrome tanned leather, the fibers are thin, as in dried, raw skin, but in the vegetable tanned leather, the fibers have grown to such an extent that they almost completely fill the interfibrillary spaces. But this difference in size of the fibers is only what one would expect from the fact that 100 grams of skin protein combined with 57.0 grams of tannin, in the case of the vegetable tanned leather, as against only 7.2 grams of chromic oxide, in the other. This difference is responsible for the greater weight and solidity of vegetable tanned leather. Either leather can be made tough and as soft as desired by the introduction of a sufficient amount of oil, but the vegetable leather is capable of

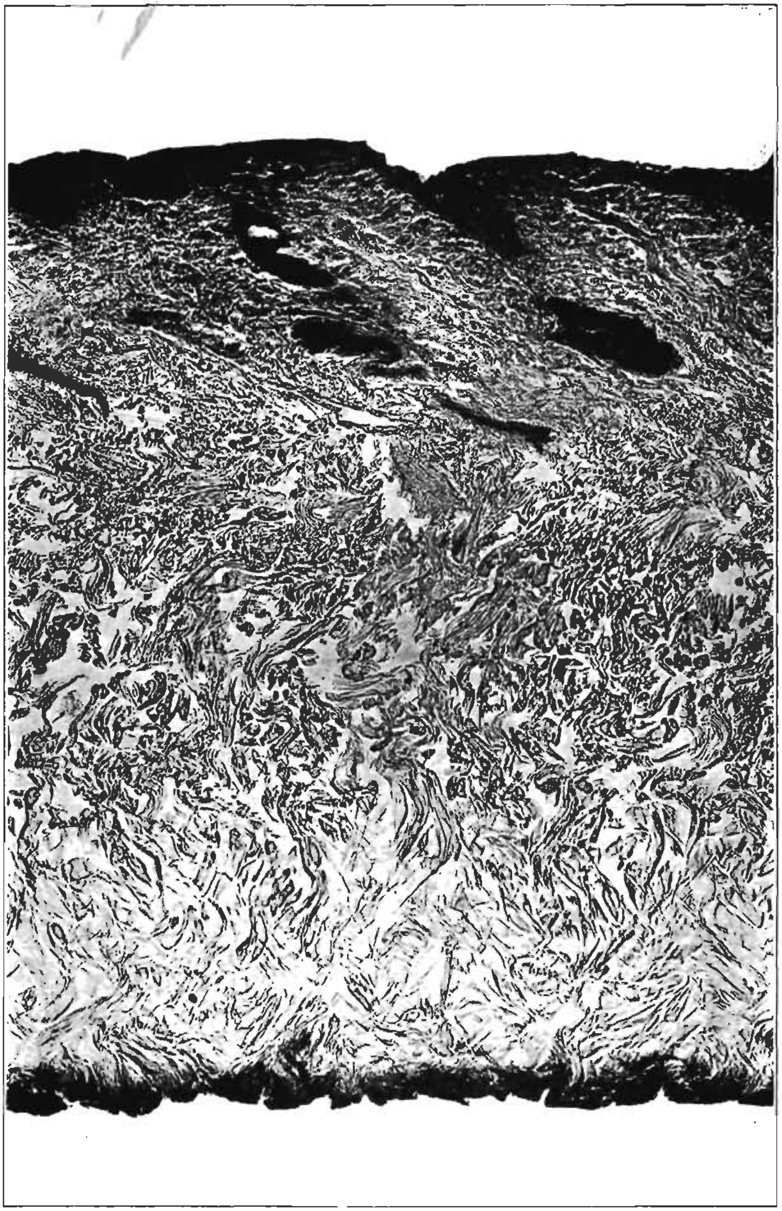


Fig. 145.—Vertical Section of Horse Leather.
(Cordovan—from shell.)

Location: butt.
Thickness of section: 20 μ.
Stain: none.
Tannage: chrome.

Eyepiece: none.
Objective: 16-mm.
Wratten filter: K3-yellow.
Magnification: 70 diameters.

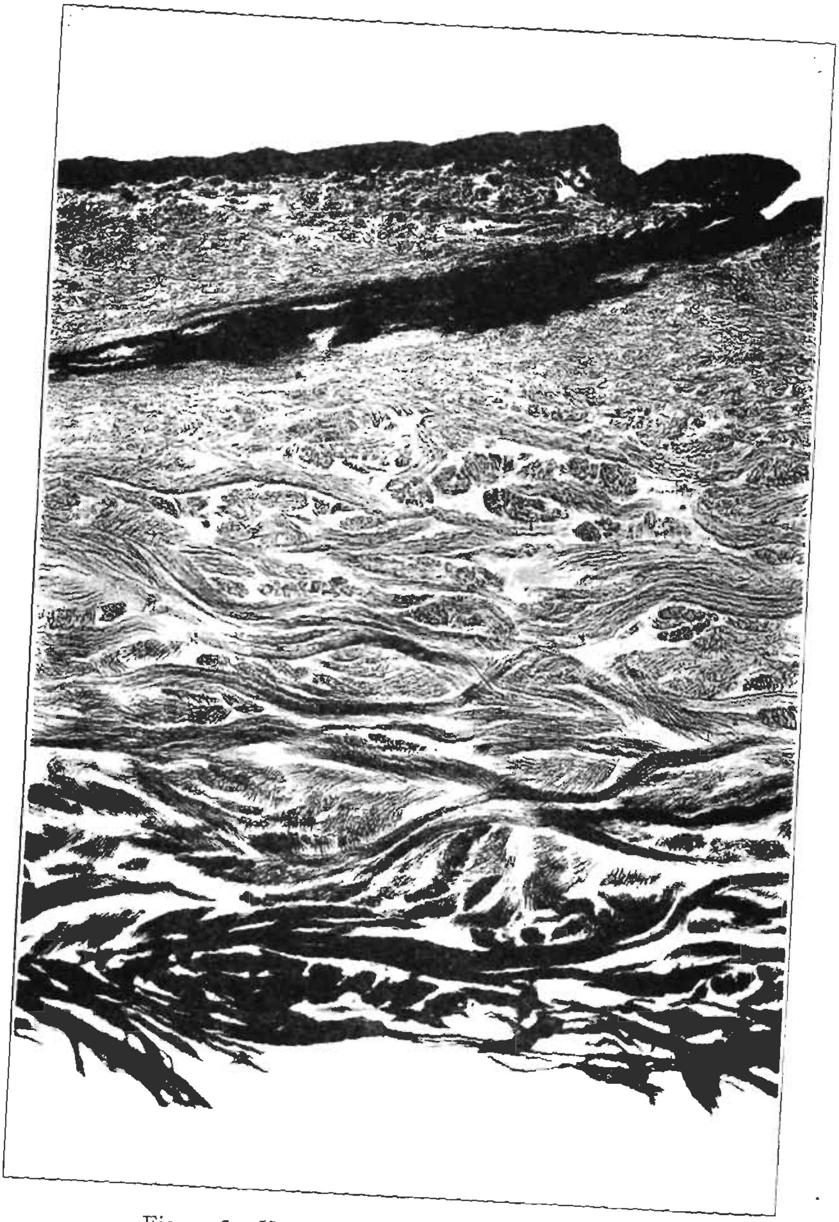


Fig. 146.—Vertical Section of Goat Leather.

Location: butt.
Thickness of section: 40 μ.
Stain: none.
Tannage: chrome.

Eyepiece: 5X.
Objective: 16-mm.
Wratten filter: H-blue green.
Magnification: 92 diameters.

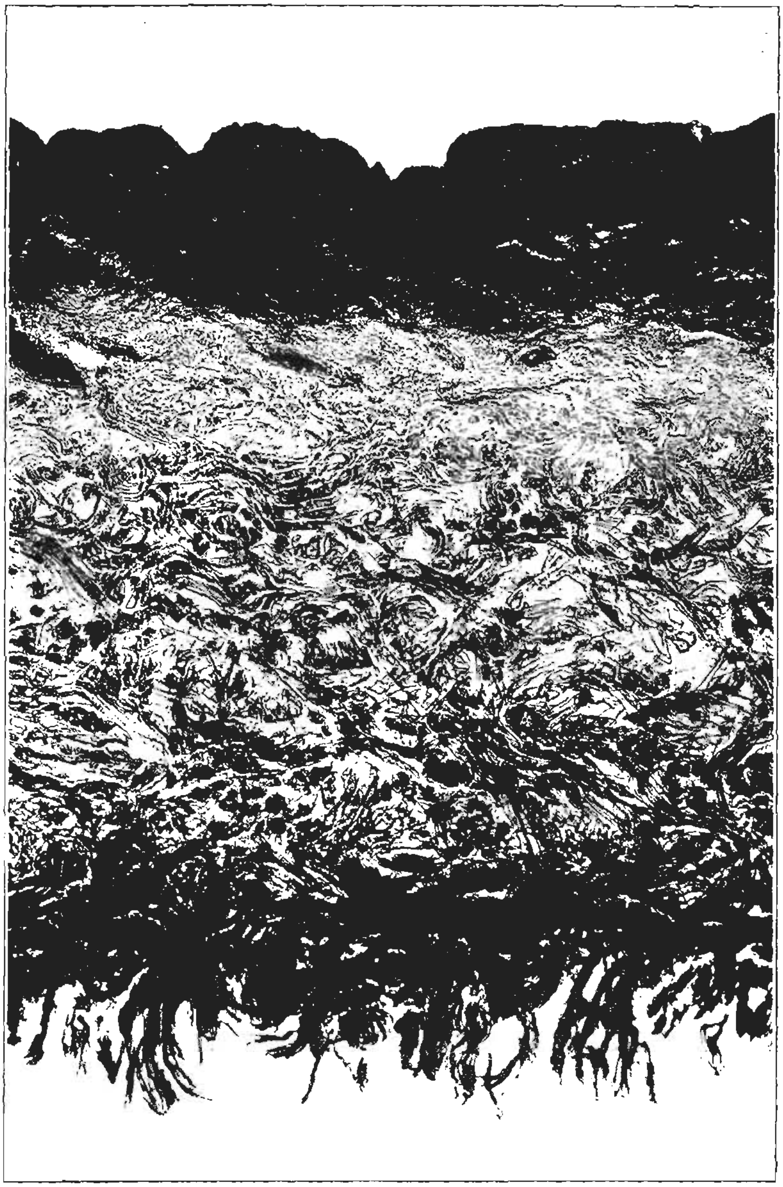


Fig. 147.—Vertical Section of Slink Calf Leather.
(Black ooze calf.)

Location: butt.
Thickness of section: 30 μ.
Stain: none.
Tannage: chrome.

Eyepiece: 5X.
Objective: 16-mm.
Wratten filter: B green.
Magnification: 105 diameters.

absorbing a much greater quantity of oil without becoming raggy. By comparison with the vegetable leather, the chrome leather feels empty.

Another outstanding difference between the two kinds of leather is the relatively high sulfuric acid content of the chrome tanned leather compared to the negligible amount present in the vegetable leather. This particular sample of leather showed by analysis 6.65 grams of sulfuric acid per 100 grams of skin protein, which is typical of leathers of this type on the market. It should be recognized, however, that this sulfuric acid is not entirely free, but is combined either with the chromium compounds or with the skin protein. Only a trace of acid is free at any one time, but as soon as this trace is removed by washing with water, more is immediately liberated by hydrolysis.

Attempts to free chrome leather from sulfuric or other mineral acid, without damaging the leather in some way, have not been successful, so far as the author is aware. Reducing the content of sulfuric acid much below that normally occurring in chrome leather seems to cause brittleness, although the cause of this is not known. In making comparative tests, the author has always found shoes made from vegetable much more comfortable, especially on long walks, than shoes from chrome leather and has attributed at least part of this difference to the hydrolyzable sulfate present in the chrome leather.

The rise of chrome tanning has been favored by its speed and comparative simplicity. The manufacture of vegetable leathers requires a much longer time and more labor. In the manufacture of light leathers, not sold by weight, tanners have naturally preferred to switch to the quicker method of tanning with chromium salts, although some of the best grades of upper leather are still tanned with vegetable tanning materials. In the manufacture of heavy leathers, sold by weight, tanners have been forced to adhere to the older method of vegetable tanning in order to get profitable yields. Incidentally, the author believes that they also get better leather.

In Fig. 145 is shown a vertical section of chromed tanned horse hide, which should be compared with Fig. 105, of Chapter 13. Both of these sections are from corresponding points of the same hide, which was cut in two after bating, half being tanned in chrome liquor and half in vegetable tan liquors, as in the experiment with calf skin. The difference between the two kinds of tannage is even more noticeable here.

Fig. 146 shows a fine specimen of chrome tanned goat skin, such as is used in making kid shoes. Fig. 147 represents an unusually fine specimen of ooze, or suede, leather. This leather is worn with the flesh side out, which gives it a velvety appearance. For the best grades, only slink skins are used because these are usually free from the blood vessels which are ordinarily abundant at the flesh boundary of the skin and detract from the appearance of leather finished on the flesh side. In comparing the various sections, any differences in magnification noted must be taken into consideration.

Theory of Chrome Tanning.

The simplest theory of chrome tanning is that it consists of the combination of chromium and collagen, forming a series of salts that might be called collagenates of chromium. From this chemical theory, there are theories of many shades and kinds all the way down to the assumption that chrome tanning consists of a precipitation of colloidal chromic oxide upon the surfaces of the skin fibers.

In following chrome tanning by means of the microscope, the author has observed the chrome liquor diffuse into the skin and also into the substance of each fiber, but without any visible sign of precipitation. When tanning was complete, each fiber looked like a transparent rod of green glass. This is similar to the phenomenon observed in vegetable tanning.

Thompson and Atkin [21] recently attempted to apply the Procter-Wilson theory of vegetable tanning to chrome tanning. The electrical charge on the collagen may be accepted as positive during chrome tanning and it seemed improbable to Thompson and Atkin that combination takes place between positively charged collagen and a positively charged chromium ion or complex. In a review of 80 papers dealing with chromium salts, they found numerous contradictions on points of importance, but one fact seemed to stand out as definitely established. Chromic sulfate exists in solution in two modifications, one green, the other violet. At any temperature between 0° and 100° C., a definite equilibrium exists between the two forms in solution, the green being more stable at high and the violet modification at lower temperatures. In the change from violet to green by raising the temperature, equilibrium is quickly reached, but in the reverse action, following a lowering of the temperature, equilibrium is reached only after a long time. Thompson and Atkin offered the theory that chrome tanning is effected by an anion or negatively charged colloidal particle containing chromium and arising from the green modification of chromic sulfate. The action would then be similar to that described in the Procter-Wilson theory of vegetable tanning.

In support of their theory, Thompson and Atkin cite a number of investigations showing that anodic migration occurred in the electrophoresis of solutions of the green modification of chromic sulfate. It was pointed out by Seymour-Jones,[22] however, that this theory would be acceptable only provided it could be shown that all chrome liquors capable of tanning contain this negatively charged chromium complex.

Bassett [23] electrolyzed solutions obtained by the reduction of potassium bichromate with sulfur dioxide. With fresh, dilute solutions, no precipitate was obtained with either barium chloride or ammonium hydroxide, indicating the absence of sulfate or chromic

[21] A Possible Theory of Chrome Tanning. F. C. Thompson and W. R. Atkin. *J. Soc. Leather Trades Chem.* 6 (1922), 207.
[22] The Electrophoresis of Chromic Solutions. F. L. Seymour-Jones. *Ind. Eng. Chem.* 15 (1923), 265.
[23] *J. Chem. Soc.* 83 (1903), 692.

ions. Bassett assumed the presence of complex chromo-sulfates of the type $\begin{matrix} KSO_3 \\ KSO_4 \end{matrix} > Cr_2(SO_4)_2$. When fresh green solutions, containing a slight excess of sulfur dioxide, were electrolyzed under dilute sulfuric acid, a green boundary moved to the anode and a violet boundary to the cathode. With lapse of time the anodic migration decreased in speed and finally ceased altogether.

Seymour-Jones points out that the cessation of anodic migration on standing is important to the theory, since it implies the breaking up of the negative complex to potassium sulfate, potassium sulfite, and chromic sulfate, and, consequently, the absence of chromium in a negative complex in ordinary chrome liquors. Moreover, if the green solution is due to chromic anion and the violet to chromic cation, pure violet solutions should not tan, according to the Thompson-Atkin theory, but Burton [24] found that the violet modification tans more rapidly than the green. This seemed a natural finding in view of the fact that Blockey [25] had previously shown that the hydrogen-ion concentration of solutions of the green modification is very much higher than that of solutions of the violet modification.

Ricevuto [26] electrolyzed a 10-per cent solution of chrome alum and observed migration only to the cathode. Upon addition of sodium hydroxide, the solution became turbid and some particles moved to the anode. When the solution was rendered alkaline, the particles moved entirely to the anode, from which Ricevuto concluded that chrome tanning is possible only in alkaline solution, which we know to be quite contrary to fact.

Seymour-Jones carried out a number of electrophoresis experiments on various chromic solutions for the purpose of testing the Thompson-Atkin theory. A U-tube was used which was provided with a stopcock in each arm a little above the bend. The chromic solution was placed in the bend below and up to the top of the stopcock. Above this was placed a 0.05-molar solution of sodium sulfate. The U-tube was connected by stoppers with electrodes in small distilling flasks, copper in saturated copper sulfate serving as the cathode and platinum in saturated sodium chloride solution as the anode. Diffusion of these solutions was prevented by cotton wool plugs. The ordinary house current of 110 volts D. C. was used, passing through a lamp filament to reduce the amperage to a convenient amount. The results are given in Table XXXVII.

Wherever chrome liquor moved to the anode, it was of a pure green color, while that moving to the cathode was of a bluish green. The basic chromic chloride, which showed no anodic migration at all, was used to tan hide powder, which it did in quite the normal manner. This proves that the Thompson-Atkin theory is not of general application and suggests that it may not hold in any case.

[24] Chrome Tanning, I. D. Burton. *J. Soc. Leather Trades Chem.* 4 (1920), 205.
[25] Investigation of One Bath Chrome Liquors. J. R. Blockey. *J. Soc. Leather Trades Chem.* 2 (1918), 205.
[26] *Kolloid Z.* 3 (1908), 114.

Seymour-Jones [27] experimented upon the ultrafiltration of basic chromic sulfate, such as is used in tanning, and found no colloidal matter. A chrome liquor was prepared by reduction of a solution of sodium bichromate with sulfur dioxide, the excess sulfur dioxide being driven off by boiling. The dark green solution contained 269.9 grams of chromic oxide per liter. This was ultrafiltered through hard filter papers impregnated with 1-per cent and 5-per cent gelatin solutions, respectively, which were subsequently hardened with 4-per cent formaldehyde solution. The solution was also ultrafiltered through a

TABLE XXXVII.

DIRECTION OF MIGRATION OF CHROMIUM UPON ELECTROLYSIS OF CHROME LIQUORS.

Solution	Concentration	Migration to
$Na_2Cr_2O_7$ reduced with SO_2. Solution 13 months old. All free SO_2 removed	239.9 grams of Cr_2O_3 per liter	Anode and Cathode
$Cr_2(SO_4)_3$. Fresh, cold, green solution	0.2-molar	Cathode only
$Cr_2(SO_4)_3$. Heated and cooled green solution	0.2-molar	Cathode only
$Cr_2(SO_4)_3$ plus NaOH to make $CrOHSO_4$	0.2-molar	Anode and Cathode
Commercial chrome crystals, basic sulfate	166.5 grams of Cr_2O_3 per liter	Anode and Cathode
$CrCl_3$ plus NaOH to make $CrOHCl_2$.	45 grams $CrCl_3$ per liter	Cathode only
Chrome alum. Fresh, cold violet solution	0.2-molar	Cathode only
Chrome alum. Heated and cooled, green solution	0.2-molar	Cathode only
Chrome alum. Heated and cooled, plus NaOH to make $CrOHSO_4$...	0.2-molar	Cathode only

collodion disc. In every case the solution passed through unchanged, no colloidal particles being retained by the filter. The same result was obtained when the solution, diluted with 3 volumes of water, was allowed to remain in a collodion bag suspended in air. The original, concentrated solution and one diluted to 10 volumes with water were dialyzed in collodion bags against water, which was changed frequently. In less than 18 hours even the concentrated solution had completely dialyzed through the membrane, the liquid remaining in the bag being colorless. This shows that we are not dealing with a colloidal dispersion in chrome tanning.

T. W. Richards and F. Bonnet [28] electrolyzed a basic chromic sulfate solution and found the migration entirely cathodic and there were 19.3 grams of Cr transported per 96,580 coulombs. From this they concluded that each atom of chromium cannot be associated with more

[27] The Colloid Chemistry of Basic Chromic Solutions. F. L. Seymour-Jones. *Ind. Eng. Chem.* 15 (1923), 75.
[28] *Proc. Am. Acad. Arts Sci.* 39 (1903), 1.

than two positive charges and probably with not more than one. Assuming that the sulfate ion alone migrates anodically with a mobility of 70, the mobility of the chromium group is 41 assuming a single charge and 243 assuming a double charge, but the latter figure appears much too high. They suggest that the cation may be $Cr(OH)_2^+$, which Siewert[29] and Whitney[30] had shown to be the most probable cation in boiled solutions of chromic chloride or nitrate.

The author's view of the mechanism of chrome tanning is as follows: Although the degree of ionization of the carboxyl groups of the protein, in which a hydrogen ion passes into solution, may become extremely small with increasing acidity, it never becomes zero. This means that, even if the electrical charge on the protein structure is predominantly positive, there still remain a relatively small number of negatively charged groups scattered throughout this structure. $Cr(OH)_2^+$, or ions of a similar nature, diffuses into the jelly composing the fibers of the skin and combines with these negatively charged groups wherever encountered. Having neutralized the electrical charges on each other, both the collagen and chromium groups become capable of ionizing further, the chromium group giving off another hydroxide group and the collagen a hydrogen ion. With a repetition of this process, all three bonds of the chromium become united directly with the collagen structure. The fundamental assumption underlying this view is that however small may be the concentration of negatively charged groups in the collagen structure under the conditions of tanning, it is very much larger than would result from the dissociation of the chromium compound of collagen.

This theory is not antagonistic to the Procter-Wilson theory of vegetable tanning, but actually supplements it. In vegetable tanning, the tannin probably attaches itself to the amino or other basic groups of the protein structure; in chrome tanning, the chromium attaches itself to the carboxyl or other acid groups. This is corroborated by the fact that chrome tanning apparently does not lessen the capacity of the skin for combination with vegetable tanning materials, or vice versa. Wood[31] found that plates of gelatin tanned with chromium were capable of combining with as much tannin as before the chrome tanning, suggesting that the chromium and tannin are not attached to the same groups in the protein structure. This is not in accord with the Thompson-Atkin theory, in which both chromium and tannin would be attached only to the positively charged groups of the protein. That the collagen undergoes a chemical change in chrome tanning is proved by the fact that it loses its property of being convertible into gelatin by contact with boiling water.

[29] *Ann. Chem. Pharm.* 126 (1863), 86.
[30] *Z. physik. Chem.* 20 (1896), 40.
[31] The Compounds of Gelatin and Tannin. J. T. Wood. *J. Soc. Chem. Ind.* 27 (1908), 384.

Chapter 15.

Other Methods of Tanning.

Of the innumerable substances capable of combining with collagen, the only ones classed as tanning agents are those whose compounds with collagen are but little dissociated, imputrescible, incapable of swelling greatly in water, and stable under ordinary condition and which cause the skin fibers to lose their tendency to glue together during drying. The suitability of a material as a tanning agent naturally depends upon its availability and cost; the simplicity of its use, and the properties of the leather which it yields. The high quality and yield of leather given by the natural vegetable tanning materials and the simplicity of tanning with chromium compounds make these two classes of materials the favorites in leather manufacture. Other materials, however, find a place in the manufacture of special types of leather, either alone or in conjunction with vegetable or chrome tanning materials.

Combination of Chrome and Vegetable Tanning.

Attempts to combine the advantages of both chrome and vegetable tanning have met with some success for certain classes of leather. During the war there was a demand for vegetable tanned leather for shoe uppers, but the length of time required for the tanning of hides to produce this leather made it impossible to meet the demand. The tanning could be done quickly enough with chrome liquors, but the resulting leather was not suitable. It was found, however, that the leather could be made to serve the purpose tolerably well by giving it a partial tannage in vegetable tan liquors after it had been completely tanned with chrome. The best example of this was the so-called chrome retan army upper leather, a vertical section of which is shown in Fig. 148. This leather was made from cow hide and was first tanned with chrome liquor and then hung in vegetable tan liquor for a few days, or until the tan liquor had penetrated more than half of the thickness of the hide. The hide was then split down to the required thickness, although the splitting was done before the retanning in some cases. The lightly colored band running across the lower half of the picture represents the inner layer of the hide to which the tan liquor did not penetrate. It appears nearer to the flesh surface only because the hide was split after retanning. It will be noted that the fibers in the retanned portions are larger than those in the pure chrome layer. At the lower left hand corner, a fiber can be

Fig. 148.—Vertical Section of Chrome-Retan Army Leather.
(Cow hide.)

Location: butt.
Thickness of section: 40 μ.
Stain: none.
Tannage: chrome plus vegetable.

Eyepiece: none.
Objective: 16-mm.
Wratten filter: K3-yellow.
Magnification: 54 diameters.

seen running from the retanned to the pure chrome layer; its size decreases noticeably.

The advantage of the preliminary chrome tanning lies in the speed with which the subsequent vegetable tanning operation may be carried out. The chrome tanned hides may be put at once into liquors stronger than usual, which hastens the rate of penetration, and it is not necessary to wait for complete diffusion, since the chrome tanning of the middle layer renders it imputrescible. The vegetable retanning adds firmness to the leather and also reduces the sulfuric acid content of the chrome leather to about half its normal value.

Alum Tanning.

The use of aluminum salts for tanning skins dates back to very early times and is still applied to some kinds of leathers and in the manufacture of some furs. It never gained the popularity accorded to chrome tanning, however, because the initial compounds formed between collagen and aluminum compounds are much less stable than the ones formed with chromium compounds. Assuming that aluminum hydroxide is a stronger acid than chromium hydroxide, our theory of chrome tanning offers a plausible explanation of this fact. It would then be more difficult for all three bonds of the aluminum to combine with collagen. Where only two bonds of the aluminum are combined with collagen, we should expect the resulting compound to be very much more readily hydrolyzed than where all three bonds are combined. After drying and storing for months, alum leathers become much more stable and resistant to washing, suggesting that the combination of the third bond of the aluminum with collagen requires a long time.

Some support is given to this view by the work of Lumière and Seyewetz [1] and of A. and L. Lumière [2] on gelatin. They studied the combination of both chromium and aluminum salts with gelatin and found maximum limiting values for the extent of combination of metal with protein, under the conditions of their experiments. They found that 100 grams of gelatin combine with a maximum of 3.6 grams of Al_2O_3 or 3.2 to 3.5 grams of Cr_2O_3. Taking 768 as the equivalent weight of gelatin and assuming that it combines with all three bonds of the chromium or aluminum, we calculate that 100 grams of gelatin would combine with 3.30 grams of Cr_2O_3 or 2.21 grams of Al_2O_3. The agreement in the case of the chromic oxide is good, but the observed amount of combined alumina is about fifty per cent greater than that calculated, which, however, would be expected if only two bonds of the aluminum combined with the gelatin.

In any case alum tanning must be conducted very differently from chrome tanning. Chrome leather is resistant to washing immediately after tanning, but if freshly tanned alum leathers are washed, aluminum salts are given up and the skins swell as in dilute acid.

[1] Composition of Gelatin Rendered Insoluble by Salts of Chromium Sesquioxide. A. L. Lumière and A. Seyewetz. *Bull. soc. chim.* 29 (1903), 1077.

[2] Action of Alums and Aluminum Salts on Gelatin. A. and L. Lumière. *Brit. J. Phot.* 53 (1906), 573.

Fig. 149.—Vertical Section of Persian Lamb Fur.

Location: (?).
Thickness of section: 30 μ.
Stain: solid brown.
Tannage: alum.

Eyepiece: none.
Objective: 16-mm.
Wratten filter: H-blue green.
Magnification: 90 diameters.

In practice the skins are tumbled in a solution of basic aluminum sulfate and enough sodium chloride to prevent undue swelling of the skin. It is sometimes desirable to add enough sodium bicarbonate to the liquor, after the alum has completely penetrated the skins, to bring it to the point at which precipitation just begins. After a few hours longer, or next day, the skins are rubbed with a mixture of egg yolk, cottonseed oil, and flour, but are not washed. They are then allowed to dry thoroughly. Sometimes the egg yolk mixture is added to the tanning bath. The skins are kept in the dried state for weeks, or months, to give the aluminum time to become permanently fixed. The skins are then soaked in water to remove the salt and are fatliquored and colored and finished according to the kind of leather required.

In tanning skins for furs, it is customary to work the alum solution into the skin from the flesh side, supplemented with oils to keep the skin soft. Work of this kind is usually done by hand and requires some skill in order to get the best results. Fig. 149 shows a section of alum tanned fur, known as Persian lamb. Skins for this fur are from specially bred lamb slinks. In this particular skin, the wool and skin were dyed black with logwood and iron salts.

Iron Tanning.

The tanning properties of ferric salts have been known for more than a century, but attempts to manufacture iron tanned leathers have met with so many difficulties that the subject still remains in the experimental stage at this late date. Procter[3] points out that part of the trouble is due to the fact that iron salts are oxygen carriers. Ferric salts readily give up oxygen to certain kinds of organic matter, being reduced to the ferrous state, in which they take up oxygen from the air, under suitable conditions, returning to the ferric state. In this way a slow oxidation of the leather occurs, with consequent deterioration.

Jettmar[4] found the greatest difficulty in iron tanning to be that of proper neutralization of the leather. If chrome leather contains too high a proportion of sulfuric acid, it becomes very brittle upon drying and assumes a very dark green color. But the proper degree of neutralization of chrome leather is a comparatively simple matter. In attempting to neutralize iron tanned leather, Jettmar found that the iron salts became colloidally dispersed and were washed out of the leather. Apparently the neutralization is necessary to bring about a permanent combination between iron and collagen, but the iron compounds pass into the colloidal state, upon neutralization, before they have had the opportunity to combine with the collagen. Since colloidal ferric oxide carries an electrical charge of the same sign as that on the collagen in acid solution, there would be no tendency for

[3] The Principles of Leather Manufacture. 2nd Edition, p. 275.
[4] Iron Tannage. J. Jettmar. *Cuir.* 8 (1919), 74, 106.

the two to combine. This difficulty was partly overcome by using a strong solution of neutral salt to prevent the formation of colloidal ferric oxide during the neutralization. The iron tanned leather was improved in quality by retanning it with formaldehyde.

Röhm [5] patented the use of the salt $FeSO_4Cl$ for tanning. It is obtained by the action of chlorine upon ferrous sulfate. Just why this salt should have unusual tanning properties is not made clear.

A good summary of much of the work done on iron tanning is contained in a paper by Jackson and Hou,[6] who carried on an extensive investigation of the tanning properties of iron salts. They pointed out that investigators generally seem to have the idea that the salt responsible for the tanning action has the formula $FeOHSO_4$, whereas this salt is not stable in solution, but invariably gives a precipitate of hydrated ferric oxide. They attribute the brittleness usually associated with iron tanned leathers to improper tanning, resulting from the precipitation of this hydrated ferric oxide. They showed that ferric sulfate is much more readily precipitable than chromic sulfate by diluting a solution of the two. With increasing dilution, there was a progressive precipitation of iron, but the chromium remained in solution.

Jackson and Hou prepared iron tanned leather which they were convinced compared favorably with other mineral tanned leathers. Its character seemed to lie between that of alum and chrome leathers. It would not stand the action of boiling water, but would shrink when brought into contact with water having a temperature above 75° C. They summarize the chief factors in their findings as follows: The iron salts must be kept in the ferric state by using an excess of a proper oxidizing agent and by means of an after oxidation. During tanning, the acidity of the liquor must be so adjusted as to give a basic salt of iron in which the ratio of equivalents of hydroxide groups to equivalents of acid radical is never less than 1:5 nor more than 1:3. Neutralization must be effected so gradually as to effect a uniform fixation of iron throughout the skin. The leather must be dried before subsequent treatment in order to minimize the reactions between free iron and materials used later that would give the leather an undesirable color.

During the war the scarcity of tanning materials forced Germany to investigate every available source, including iron salts, and had the war continued long enough, she might have been forced to produce iron tanned leathers on a large scale. But, unless iron leathers are produced which are at least the equal of chrome leather, it is doubtful that they will ever be made on an extensive scale, except in cases of emergency, because the total cost of tanning material used in making chrome leather is small compared to the loss in selling price that would result from even a very small depreciation in quality of the leather.

[5] British Pat, 146,214, June 26, 1920.

[6] *Iron Tannage.* D. D. Jackson and T. P. Hou. *J. Am. Leather Chem. Assoc.* 16 (1921), 63, 139, 202, 229.

Tanning with Silicic Acid.

Like tannin, colloidal silicic acid is negatively charged and precipitates gelatin from solution. In 1862 Thomas Graham[7] studied the precipitation of gelatin by silicic acid and reported as follows: "Silicate of gelatine falls as a flaky, white and opaque substance, when the solution of silicic acid is added gradually to a solution of gelatine in excess. The precipitate is insoluble in water and is not decomposed by washing. Silicate of gelatine, prepared in the manner described, contains 100 silicic acid to about 92 gelatine. In the humid state the gelatine of this compound does not putrefy. When a solution of gelatine was poured into silicic acid in excess, the co-silicate of gelatine formed gave, upon analysis, 100 silicic acid with 56 gelatine."

This experiment inspired Hough[8] to experiment with silicic acid as a tanning agent. He found that a purified silica sol is much too easily precipitated to be of any value as a tanning agent, but finally prepared a solution of silicic acid capable of tanning by adding a thirty-per cent solution of sodium silicate to a thirty-per cent solution of hydrochloric acid until the concentration of free acid was reduced to decinormal. If the acid is poured into the sodium silicate solution, the silica will be precipitated when the neutral point is approached; the silicate must always be poured into the acid solution whose strength must not be allowed to fall below decinormal. The tanning proceeds a little faster than is the case with vegetable tanning, light skins being fully tanned in from 3 to 5 days, and heavy bull hides in about a month. The leather usually contains from 17 to 24 per cent of silica; in fact one of the difficulties of the process is to prevent too great a combination of silica with the skin protein. The leather is pure white and may be finished like ordinary chrome leathers.

Hough attributes the failure met with in attempting to combine silica and vegetable tanning to the fact that both the silica and tannin are negatively charged and tend to combine with the same amino groups of the collagen structure. On the other hand, good leathers were produced by a combined silica and alum tannage, probably because the alum attaches itself to the carboxyl groups of the collagen. The presence of alum, however, seemed to retard the tanning, possibly on account of the condensation of aluminum silicate on the surface of the skins hindering the penetration. But by giving the skins a preliminary chrome tannage and then putting them into the silica liquors, the rate of tanning was increased and the final leather had greater solidity and firmness.

In discussing the evolution of the different methods of tanning, Thuau[9] states that one serious fault with silica tanning is that the leather, after keeping for a few months, tears very easily, probably because of the action of the silicic acid on the leather fibers. If

[7] *J. Chem. Soc.* 15 (1862), 246.
[8] Tanning with Silica. A. T. Hough. *Cuir.* 8 (1919), 209, 257, 314.
[9] Evolution of the Different Methods of Tanning. U. J. Thuau. *Cuir.* 9 (1921), 10, 80, 102.

this difficulty could be overcome, he predicts that the process might supplant chrome tanning.

Miscellaneous Mineral Tannages.

Sommerhoff [10] claims to have discovered that certain insoluble sulfides, silicates, hydroxides, and phosphates of the heavy metals have a marked tanning effect on skin, when freshly precipitated or colloidally dispersed. In one experiment, copper sulfate was precipitated with disodium phosphate. The jelly-like precipitate was filtered off and then suspended in water and shaken with a piece of hide, which became completely tanned in about two hours. The leather contained about 13 per cent of ash. Whether Sommerhoff really obtained a tanning action is difficult to determine from his paper, but the subject seems not to have been carried very far.

Garelli [11] found that the tanning properties of cerium chloride are much like those of aluminum salts, provided the solution used for tanning is made sufficiently basic and dilute. With properly adjusted conditions, he obtained a pliable, white leather containing about 9 per cent of Ce_2O_3. Garelli and Apostolo [12] were not so successful in attempting to tan skin with salts of bismuth. If any compound between the bismuth and collagen were formed, it was unstable, the skin returning to the raw condition upon washing in cold water.

The experiments of Apostolo [13] seem to indicate that freshly precipitated sulfur has tanning properties. He added a small amount of lactic acid to a concentrated solution of sodium thiosulfate, which became turbid, due to the precipitation of sulfur. Into the turbid solution he put a piece of skin, which apparently absorbed all of the free sulfur. The skin was withdrawn long enough to add a little more acid to liberate more sulfur. The skin was returned to the liquor and it again absorbed all of the sulfur in suspension. This was repeated a number of times, care being taken to avoid using acid in excess of the amount of sodium thiosulfate present. The leather obtained is described as white, extraordinarily soft, and of beautiful appearance. It did not swell when left for 24 hours in cold water, and when dried and stretched again had lost none of its quality. The leather gave up only 1 per cent of sulfur to carbon disulfide and this seemed to have been merely mechanically held, as the remaining skin seemed still to be fully tanned, and contained 2.5 to 3.5 per cent of sulfur. The leather was decomposed, however, when brought into contact with hot water.

Meunier and Seyewetz [14] made the rather startling discovery that chlorine and bromine have tanning properties. Plates of gelatin are

[10] The Tannage of Hide by Means of Insoluble Metallic Jellies. E. O. Sommerhoff. *Collegium* (1913), 381.

[11] Tanning by Means of Cerium Salts. F. Garelli. *Collegium* (1912), 418.

[12] Action of Bismuth Salts on Skins. F. Garelli and C. Apostolo. *Collegium* (1913), 422.

[13] Tanning of Hides with Freshly Precipitated Sulfur. C. Apostolo. *Collegium* (1913), 420.

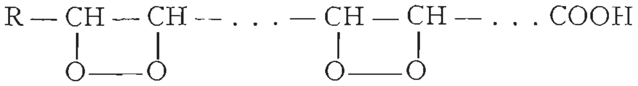
[14] New Studies Dealing with the Tanning of Gelatin and of Skin. L. Meunier and A. Seyewetz. *Collegium* (1911), 373.

rendered insoluble by contact with aqueous solutions of either bromine or chlorine, in the presence of salt to prevent swelling. The gelatin evidently combines vigorously with either element. Raw skin was found to be affected similarly. Iodine had no such effect on either gelatin or skin. The authors suggested the use of chlorine or bromine as a preservative for skin and also as a tanning agent to be used prior to tanning by other methods for all kinds of skins. The leather obtained is absolutely imputrescible and resistant to cold, but not boiling, water.

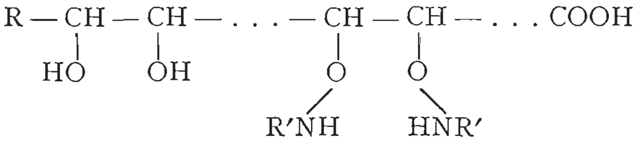
Tanning with Oils.

One of the commonest examples of oil tanned leather is the ordinary chamois leather. This is made from the reticular layer of sheep skin, which is split from the grain layer so that the two may be tanned separately for very different purposes. The flesh splits are soaked with cod oil and pummeled in specially designed machines in order to assist the penetration of the oil. A combination of oil with the skin protein takes place with the evolution of acrylic aldehyde and other pungent products and the development of a considerable amount of heat. Oxidation of the oil occurs simultaneously. The pummeling, or stocking, is stopped occasionally and the skins are spread out to cool off, after which the stocking is continued. The completion of the process can only be determined by practice. After tanning, the splits are soaked for a few hours in warm water and then pressed to remove uncombined oil, which is sold under the name moellon degras. The oil still adhering to the skins is removed by washing with a solution of sodium carbonate. The skins are then bleached in strong sunlight.

The nature of the combination of oils with collagen has been studied by Fahrion[15] and by Meunier.[16] According to Fahrion, the unsaturated, free fatty acids are the active tanning agents of the fish oils in chamoising. The active acids have at least two double bonds and upon oxidation they assume a peroxide structure represented by the formula



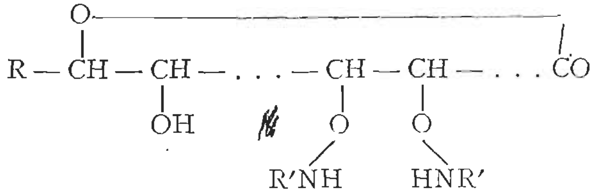
Representing collagen by the simplified formula $R'NH_2$, the combination of oxidized fatty acid and collagen, according to Fahrion's view, would yield the following compound:



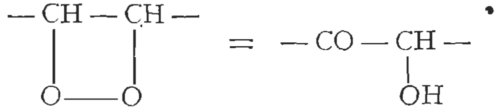
[15] Theory of Leather Formation. W. Fahrion. *Z. angew. Chem.* (1903), 665; (1911), 2083.

[16] Modern Theories of the Various Methods of Tanning. L. Meunier. *Chimie & industrie* 1 (1918), 71, 272.

He considers that this combination is followed by a conversion into the lactone



and that only a portion of the peroxide acids enter into combination with the protein matter, the rest being converted by molecular rearrangement into hydroxy-acids, thus



These hydroxy-acids are then converted into lactones which are retained by the fibers, being resistant to the alkaline washing which completes the manufacture of chamois leather. The aldehydes formed in the process probably also exert a tanning action on the skins.

According to Meunier, the tanning power of fish oils is due to the presence of free fatty acids possessing four double bonds of which at least two are capable of combining with oxygen to give the peroxide structure shown above. Thus if a skin, previously dehydrated with alcohol, be treated with an alcoholic solution of oleic acid, a soft leather is obtained, but after draining off the alcohol to remove the excess of oleic acid, the skin does not show any sign of being tanned when placed in water. Substituting the fatty acids of rape oil for oleic, a yellow leather somewhat more resistant to the action of water is obtained. These acids belong chiefly to a series possessing two double bonds and include a little linolenic acid, with three double bonds. Substituting the fatty acids of linseed oil, rich in linolenic acid, the leather obtained is still more resistant to water, but is not the equal of that made from the fatty acids of cod oil possessing four double bonds.

Tanning with Aldehydes and Quinones.

Payne and Pullman [17] patented the use of formaldehyde as a tanning agent in 1898. Since then a number of investigators have studied the action of various aldehydes upon gelatin and skin protein. Some aldehydes, like benzaldehyde, show little or no tanning power. The use of formaldehyde has frequently been suggested as a means of preparing skins for tanning with vegetable tanning materials by the newer rapid methods, in which stronger tan liquors are used. The formaldehyde adds very little weight to the leather, but its combina-

[17] British Pat. 2872, Feb. 4, 1898.

tion with skin prior to vegetable tanning lessens the astringency of the tan liquor and increases its rate of diffusion into the skin.

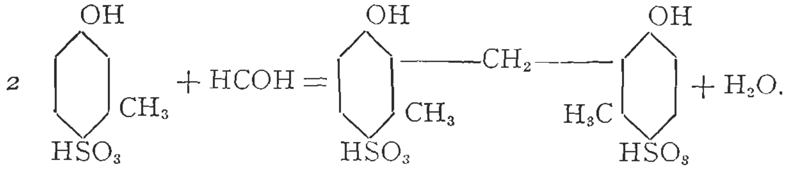
Hey [18] observed that formaldehyde has tanning properties only in solutions having a pH value greater than 4.8 and that the best practical results are obtained when the pH value lies between 5.5 and 10.0. At higher pH values the skin becomes swollen and the surface becomes almost impermeable to the formaldehyde not combined with the skin at the surface. Meunier suggests that oxidation of the skin proteins, affecting the amino groups, precedes combination with either aldehydes or quinones, whose tanning properties were discussed in Chapter 13. When quinone combines with skin protein, part of the uncombined quinone is reduced to quinol, which Meunier attributes to the oxidation of protein.

Meunier also studied the action of gallic acid, naphthols, quinol, *pyrogallol, diaminophenol hydrochloride, and resorcinol upon gelatin.* When these substances are dissolved in dilute solutions of sodium carbonate and exposed to air, they act slowly upon gelatin, rendering it insoluble in boiling water. Without access to the air, however, this action is not obtained.

Tanning with Syntans.

In vegetable tanning, in slightly acid solution, combination takes place between positively charged protein and negatively charged colloidal particles of tannin. A distinct advance in the science of tanning was made when Stiasny [19] discovered that water soluble products can be obtained by mixing phenolsulfonic acids with formaldehyde, under the right conditions, in which the particles formed are negatively charged in acid solution, precipitate gelatin dispersions, and possess marked tanning properties. Equal parts of cresol and sulfuric acid are heated, with stirring, for two hours, the temperature being kept at about 105° C. The mixture is then cooled to 35° C. and 1 molecule of formaldehyde is added for each molecule of cresol present. The important point to be observed is that the formaldehyde must be added very slowly and the temperature must not be allowed to rise above 35° or the ordinary insoluble products may be obtained.

According to Grasser,[20] the reaction proceeds as follows:



Besides cresols, naphthalenes and higher hydrocarbons are also used in the preparation of these synthetic materials, now commonly called

[18] Formaldehyde Tannage. A. M. Hey. *J. Soc. Leather Trades Chem.* 6 (1922), 131.
[19] A New Synthetic Tannin. E. Stiasny. *Collegium* (1913), 142.
[20] Synthetic Tannins. G. Grasser. English translation by F. G. A. Enna. Crosby Lockwood & Son, London (1922).

syntans. For an interesting discussion of these, the reader is referred to Grasser's recent book.

Raw skin can be tanned by simply immersing in a pure solution of these syntans, provided the concentration and acidity are properly adjusted. With decreasing acidity, they seem to lose their tanning properties. A typical commercial syntan preparation examined by the author showed a titrable acidity of 0.65 gram equivalents per liter and a pH value of 0.63. Grasser found that concentrated solutions of Neradol D, the original syntan, actually cause a gelatinization of raw skin, which might have been expected from its high acidity. But when used at sufficient dilution, no ill effects were observed at all and a tough, white leather was obtained. Since syntans add much less weight to skin than natural vegetable tanning materials, they are seldom used alone, but appear to have valuable properties when used in conjunction with other materials for certain kinds of leather.

Like formaldehyde and quinone, syntans act upon skin in such a way as to lessen the astringent effects of strong tan liquors upon it. Syntans, having a lower molecular weight than tannins, diffuse into the skin at a much greater rate and also combine with it. This partial tannage lessens the rate of combination of the tannin with the skin, thereby increasing its rate of diffusion. The syntan solution may be used as a drench for deliming the skins prior to vegetable tanning or may be added directly to the tan liquors. Like any strongly acid material, however, it must be used with caution and proper control.

The high acidity of ordinary syntan solutions makes them suitable for the bleaching of leather, the color of the leather becoming lighter with increasing acidity, or decreasing pH value, within limits.

Another valuable property of these syntans is their power to effect the solution of phlobaphenes and other difficultly soluble tannins. Grasser found that the phlobaphenes of quebracho were rendered soluble by solutions of Neradol D or sodium phenolsulfonate, but not by the free sulfonic acid. The action of the sodium salt, however, may be attributed at least partly to the pH value of its solution, since the author found phlobaphenes to be very soluble at pH values above 7. Since the phlobaphenes are probably oxidized tannins, it is possible that the syntans exert a reducing action upon them, but the real nature of the action is not known.

The method of determining the extent of penetration of Neradol D in tanning is to wash a strip of the skin, make a cutting, wash the cut portion, and then treat it with a few drops of dilute ferrous ammonium sulfate solution, which color the tanned layers a deep blue.

Another material that should be mentioned in connection with syntans is the waste sulfite liquor from the paper mills, known as sulfite cellulose. This material, purified for tanning purposes, is sold under the name of spruce extract. The active tanning agent of this material appears to be the free lignosulfonic acids. Spruce extract possesses undoubted tanning properties, but does not yield a satisfactory leather when used alone in the ordinary way. But when mixed

with other materials, such as quebracho extract, it acts much like many natural vegetable tanning materials. Its very low costs finds it a place as a filler in the manufacture of sole leather. Hill and Merryman[21] describe a method of increasing the filling properties of spruce by the use of syntans. Sole leather is first soaked in a concentrated solution of spruce and then drummed with a solution of syntan. They claim that the spruce is precipitated inside of the leather by the syntan, greatly increasing the weight and at the same time brightening the color and lessening the need for bleaching.

The chemist has almost unlimited possibilities before him in the development of new materials to supplement the ever diminishing supply of natural tannins.

[21] Some Applications of Synthetic Tanning Materials. J. B. Hill and G. W. Merryman. *J. Am. Leather Chem. Assoc.* 16 (1921), 484.

Chapter 16.

Finishing and Miscellaneous Operations.

The mere conversion of raw skin into leather does not, as a rule, make it suitable for the various purposes for which leather is used. For some kinds of leather, more work is required in the operations following the actual tannage than in the tanning and all preceding operations put together. Each of the innumerable kinds of finished leather requires a special series of operations after tanning and nothing short of an encyclopedic work could adequately treat the details of operations, even for the commoner leathers. For this reason, the following brief treatment is limited to the fundamental principles underlying the few general processes common to large classes of leathers.

Bleaching.

In vegetable tanning there is often a deposit of phlobaphenes or of ellagic acid on the surfaces of the leather which, if left there, would interfere with the coloring of the leather, giving rise to irregularities. It also frequently happens that the color of the leather becomes dark through oxidation and this may not be entirely uniform over the surface of the leather. Bleaching is a process designed to give the leather a lighter and more uniform color before it is sent to be dyed and fatliquored. It usually consists in giving the leather a bath first in a dilute alkaline solution and then in an acid one, sodium carbonate and sulfuric acid generally being used for the purpose.

When the leather is soaked in dilute sodium carbonate solution, the phlobaphenes and ellagic acid pass into solution, being soluble at pH values greater than 7. At the same time the tannins are stripped from the surfaces of the leather; it was shown in Chapter 13 that this stripping action proceeds at an increasing rate as the pH value is increased above 8. The sodium carbonate solution is usually allowed to act for only 10 or 15 minutes and the leather is then rinsed to free it from the soluble products on the surface. It is then treated with a dilute solution of sulfuric acid, which checks the action of the sodium carbonate and at the same time lightens the color of the remaining fixed tannins by lowering the pH value, the color being a function of pH value, as pointed out in Chapter 11. In this way the grain surface is cleared and the color brightened. After the bleaching, it is customary to replace the tannin lost from the surface by giving the leather a short tannage in clear tan liquor.

The use of sulfuric acid in bleaching leather has been condemned on the ground that it slowly destroys the leather, if not subsequently removed. When sulfuric acid is present in vegetable tanned leather in excess of 1 per cent of the weight of the leather, the leather may look all right for two or three years, but gradually deteriorates and in time will become as tender as blotting paper. The tanner usually takes care that the amount of acid used is not excessive or counteracts it by using an alkaline fatliquor, which neutralizes any acid left in the leather. Other bleaching agents sometimes employed are sodium bisulfite, organic acids, and syntans.

Stuffing and Fatliquoring.

Although the tanning of skin lessens the tendency for the fibers to glue together upon drying, it does not lubricate them so that they slip easily over one another. In fact, when leather is dried after tanning, without further treatment, it is usually very stiff and will crack upon bending sharply. In order to give it the desirable softness and pliability and to increase its tensile strength and resistance to tearing, oils and greases are incorporated into it to lubricate the fibers.

The amount of oil added to leather varies greatly according to the use to which the leather is to be put. In sole leather, where stiffness is desired, only 2 or 3 per cent of sulfonated oil is used and this is often added along with the concentrated tan liquor or other material used to fill and weight the leather. Waxed leathers, used for waterproof shoes, may contain as high as 30 per cent of oils, waxes, and stearin.

The direct application of oils and greases to leather, either by hand or by drumming in the molten greases, is known as stuffing and is used where it is desired to incorporate a large amount of grease into the leather. Where only a small amount of oil is desired in the leather and it is essential to have it fairly uniformly distributed, it is best to apply the oil in the form of an emulsion, in which case the process is known as fatliquoring.

In dry stuffing, the dried leather is treated with hot, molten greases, which penetrate rapidly. This method is suitable only where it is desired to have a finished leather containing upwards of 20 per cent of grease. For leathers with less grease, it is preferable to apply the greases to the wet leather. In belting leather, for example, it is customary to swab a mixture of cod oil and tallow over the surfaces of the leather while thoroughly wet. The leather is then hung in a drying chamber in which the temperature is gradually raised. As the water passes out of the leather, the oil and tallow diffuse in. When a small amount of oil is rubbed onto dry leather, the surface tends to remain oily, but when applied to wet leather, the surface of the leather after drying is not oily. For this reason it has been assumed that the evaporation of water from the leather draws the oil into the leather, but this view has been contested by

Moeller [1] who considers the action of oils upon wet leather as similar to that of cod oil in chamoising. According to his view, the vegetable tanning material causes an oxidation of the unsaturated fatty acids, as indicated by the formation of oxidized acids and the simultaneous disappearance of water from the leather, water presumably being essential to the reaction. The oxidized fatty acids then act as a tanning agent. When dry leather is oiled, this action proceeds so slowly that the leather always remains oily, whereas wet leather, after oiling, dries without retaining the oily condition.

The effect of grease in increasing the tensile strength of leather was demonstrated in a special investigation by Whitmore, Hart, and Beck,[2] who found that a petrolatum-paraffin mixture was quite as effective as the commoner cod oil-tallow mixture. Bowker and Churchill [3] showed that grease in excess of a certain amount does not add to the tensile strength, but may actually decrease it. This agrees with some observations made by the author in the stuffing of strap leather, in which the tearing strength decreased with increase of grease content above 21 per cent.

Light leathers, such as those for shoe uppers, are fatliquored rather than stuffed because fatliquoring leaves the grain surface in a much better condition for coloring. The common emulsifying agents are sulfonated oils, soaps, and moellon degras, the by-product from the manufacture of chamois leather. For a review on the literature of emulsions, the reader is referred to the paper by Thomas.[4] In the manufacture of chrome leathers, it is sometimes necessary to neutralize a portion of the sulfuric acid of the leather before applying the fatliquor, which is done by drumming the leather in a calculated quantity of sodium bicarbonate or borax solution. A fatliquor may be made simply by shaking a mixture of sulfonated neatsfoot oil, neutral neatsfoot oil, and hot water. Or the sulfonated oil can be replaced by soap and moellon degras. Van Tassel [5] proposed the use of stearamid as an excellent emulsifying agent in making fatliquors. Larger quantities of fatliquor are used for vegetable tanned leathers than for chrome. A finished chrome leather generally contains from 4 to 8 per cent of oil against from 10 to 15 per cent for vegetable tanned upper leathers.

The skins are thoroughly wet with hot water and drummed with a small volume of hot fatliquor for about half an hour, at the end of which time practically all of the oil should be separated from the solution. It has often been thought that the oil globules actually penetrate the leather during fatliquoring, but Albert F. Gallun Jr., in

[1] On the Theory of the Processes Involved in the Oiling of Leather. W. Moeller. *Gerber* 45 (1919), 277.

[2] The Effect of Grease on the Tensile Strength of Strap and Harness Leathers. L. M. Whitmore, R. W. Hart, and A. J. Beck. *J. Am. Leather Chem. Assoc.* 14 (1919), 128.

[3] Effect of Oils, Greases, and Degree of Tannage on the Physical Properties of Russet Harness Leather. R. C. Bowker and J. B. Churchill. Bureau of Standards, Technologic Paper No. 160 (1920).

[4] A Review of the Literature of Emulsions. A. W. Thomas. *J. Ind. Eng. Chem.* 12 (1920), 177.

[5] A New Emulsifying Agent and Its Application to Tannery Practice. E. D. Van Tassel, Jr. *J. Am. Leather Chem. Assoc.* 9 (1914), 236.

an unpublished work, showed that they do not do so. By splitting skins into layers immediately after fatliquoring, he found by analysis of each layer that the oil had not penetrated a measurable distance. Upon drying, however, the oil slowly diffuses into the interior and tends, in time, to distribute itself uniformly throughout the skin. The author split a skin into five layers after it had been dried after fatliquoring and found the highest percentages of oil in the outermost layers and the lowest in the layer just under the grain surface. This is probably due to the fact that the fibers of the flesh side of the skin offer more surface to the oil globules than the grain surface and hence the greater portion of the oil adheres to the flesh side.

The discussion of the stability of colloidal dispersions given in Chapter 5 may be applied to fatliquoring. The oil globules possess a negative electrical charge which gives the surface film of solution surrounding each globule an electrical difference of potential against the bulk of solution. The condition of leather to be fatliquored may be taken as that of leather in equilibrium with a solution having a pH value of from 4 to 5. The leather thus carries a positive electrical charge. The effect of putting such leather into a fatliquor, although similar in some respects to the immersion of skin in a vegetable tan liquor, is very different in at least two ways: the oil globules are very much larger than tannin particles and are not stable at pH values much below 6. The negatively charged globules will tend to combine with the positively charged leather and there may actually be some combination. But the emulsion is quickly broken up by the soluble matter present in the leather. The stability of the emulsion may be increased by making it more strongly alkaline, but this must be done with extreme caution or the leather will be ruined by overneutralization.

Experience shows that the more quickly the emulsion is broken up during fatliquoring, the greater the difficulty of getting a uniform distribution of the oil throughout the leather upon drying. For this reason the water soluble matter contained in leather to be fatliquored may exert a detrimental effect. The soluble tanning matters remaining in the leather have a tendency to break up the emulsion and, if present in too great an amount, may break the emulsion before the fatliquor has had time to serve its purpose properly and the leather will dry hard and crack easily. On the other hand, a leather practically free from soluble matter takes the fatliquor so well that it may become too soft after drying unless a smaller amount of oil is used in fatliquoring than is applied to leathers containing much soluble matter.

Penetration of Dispersions through Grain Surface.

It is interesting to note how small the particles of a dispersion would have to be in order to pass between the fibers constituting the grain surface of the leather, without distortion and assuming they could pass without coalescing or combining with the leather. Fig. 150 shows a horizontal section of vegetable tanned calf skin comprising the grain surface. The view is that looking down on the uppermost sur-

Fig. 150.—Horizontal Section of Calf Leather.
(Grain surface of leather.)

Location: butt.
Thickness of section: 15 μ.
Stain: indigo carmine.
Tannage: vegetable.

Eyepiece: 5X.
Objective: 8-mm.
Wratten filter: F-red.
Magnification: 300 diameters.

face which has been cut away from the leather below it at a thickness of less than 15 microns. (The exact measurement of thickness could not be made because this was the first cutting of the paraffin block at 15 microns that included any leather at all and was taken so as not to lose the upper surface.) The section was stained for 2 minutes in a 1-per cent solution of indigo carmine. The specimen was taken from a skin about to be fatliquored.

The average distance between the fibers of the surface is about 2 microns. If size of particle alone counted, it would merely be necessary to prepare the dispersion so as to get particles having a diameter less than this. The large empty spaces in the figure are the openings of the empty hair follicles. In the ordinary course of fatliquoring, these probably become filled with oil as soon as the emulsion breaks.

Fatty Acid Spews.

Sometimes when finished leathers are chilled, the surface becomes coated with a white crystalline deposit resembling a thin film of snow. This deposit, known to the trade as spew, usually consists of saturated fatty acids having a high melting point. For this reason, many tanners try to avoid the use of oils containing much stearin or free stearic or palmitic acids. Where sulfonated oils have been used, the deposit may contain sulfonated fatty acids, which are more difficult to remove from the surface of the leather than pure stearic or palmitic acid. Although the spew does no harm to the leather, it is undesirable because it detracts from its appearance. Its removal, however, is a comparatively simple matter and may be effected by wiping the surface with a cloth wet with naphtha or with a soap solution.

Fahrion [6] found that the splitting of a fat, with the liberation of saturated fatty acids, is not the only cause of spew of this kind. Glycerides may appear on the surface of leather which have a lower melting point than those left in the leather. But when the fatty acids are liberated from the spew, they are found to have a higher melting point and a greater tendency to crystallize than the fatty acids liberated from the glycerides remaining in the leather. A glyceride mixture is likely to cause spewing if another mixture can be separated from it by fractionation which has a lower melting point, but a higher content of saturated fatty acids. He points out that the less the tendency of a fat to crystallize, the more suitable it is for purposes of fatliquoring.

When fatliquors containing saturated fatty acids are used, the danger of spewing can be greatly lessened by incorporating in the fatliquor materials like mineral oils or sulfonated castor oil. These remain liquid at ordinary temperatures and are solvents for the fatty acids and glycerides which form ordinary spews.

When a piece of finished leather spews, it is often noted that the greatest deposits of fatty acids occur where the leather is thinnest. This is due simply to the fact that leathers fatliquored in the ordinary way have a higher total fat content in the thin parts than in the heavier

[6] Properties of Fat in Leather. W. Fahrion. *Gerber* 43 (1917), 123.

regions. In fact the fat content of the various parts may be taken as inversely proportional to the thickness. This is easily explained by the fact that the oil globules are deposited only on the surfaces of the leather during fatliquoring. Equal areas of leather thus receive the same amount of oil. If the butt is twice as thick as the shanks, it will receive only half as much oil per unit volume. For the same reason, if a very thick skin is fatliquored along with a very thin one, the thick one will not get enough oil, while the thin one will get more than its share.

A type of spew less common, but more difficult to remove, than that made up of saturated fatty acids is the resinous spew caused by the oxidation of unsaturated fatty acids in the leather. If a vegetable tanned leather contains much soluble tanning material, the tendency for the free tannin to absorb oxygen from the air increases upon fatliquoring due to the resulting increase in pH value. The oxidized tannin seems to give up its oxygen readily to the unsaturated fatty acids of cod and similar oils. The higher the pH value of the solution in the leather and the greater its content of free tannin and oxidizable fatty acids, the greater will be the danger of the formation of resinous spews, consisting of oxidized fatty acids.

Most tanners appreciate that it is undesirable to allow a large amount of soluble neutral salts to remain in the finished leather and, since such salts are easily washed out during the process, there is no good reason why they should not be removed before finishing. Nevertheless leathers are occasionally found on the market showing a deposit of salt crystals on the surface, resembling spew. It is, of course, an easy matter to differentiate between such salt deposits and ordinary fatty spews.

When leather is kept in a cool, damp place for a long time, it is apt to be subject to the growth of molds. Sometimes these show the light green color of the common mold *penicillium glaucum,* but often they appear like a white, powdery deposit, resembling the spew sometimes occurring on leathers fatliquored with sulfonated neatsfoot oil.

Coloring.

Leather is dyed either before or after the fatliquoring process, depending upon the kind of leather produced and the nature of the other operations. Natural dyestuffs are still employed for coloring some kinds of leather, but have been largely supplanted by artificial products. In coloring vegetable tanned leather, basic dyestuffs are usually preferred because they combine readily with tannin and give more intense shades than the acid dyestuffs.

When vegetable tanned leathers are to be colored with basic dyestuffs, they must first be washed so that no free tannin will diffuse into the dye bath, where it would be precipitated by the dye and tend to cause spottiness and discoloration of the leather. The leather is sometimes given a short rinsing in sodium carbonate solution in

order to free the grain surface from precipitated tannin and to strip off any excess of fixed tannin, the object being to get clearer and more uniform coloring. The leather is then drummed in a solution of a salt of titanium or antimony, such as titanium potassium oxalate or antimony potassium tartrate, which serves the double purpose of acting as a mordant and of precipitating any remaining free tannin that might otherwise diffuse into the dye bath. The leather is then given a thorough washing and is then drummed in a solution of the dyestuff. Since basic dyestuffs are precipitated by hard waters, where these must be used, they should first be acidified with acetic acid, which will prevent precipitation.

An objection to the use of acid dyes is the fact that strong acids are necessary to develop the color. The sulfuric acid often used exerts a detrimental effect upon vegetable tanned leathers, if not neutralized after coloring. Where later neutralization is objectionable, it is much better to use formic acid to develop the color since this acid appears to have no harmful effects whatever, if not used in excess. It has often been stated that acid dyes are faster to light than basic ones, but this is not uniformly true for leather.

Chrome leather may be dyed in a manner similar to that of vegetable tanned leather if it is first given a light surface retanning with a vegetable tanning material, such as gambier or sumac. The leather, after tanning and neutralizing, is drummed for a short time in a dilute tan liquor, washed, and then mordanted with a titanium or antimony salt, washed again and finally colored, after which it is fatliquored. Where the fatliquoring may cause a bleeding of the color, the dyeing must follow the fatliquoring.

By the use of acid dyestuffs, chrome leather may be dyed directly, without the necessity for a vegetable retanning. In this case, however, either the fatliquoring must be done before the coloring or else the color must be fixed in some way before fatliquoring. One method of accomplishing this is to divide the coloring operation into two parts, the leather being dyed first with an acid dye and then with a basic dye. Since the two kinds of dyestuffs coprecipitate each other from solution, forming insoluble lakes, they show little tendency to bleed into the fatliquor.

Direct colors may be used on either chrome or vegetable leathers. Alizarine and developed dyes find a use in the coloring of chrome leather. Sulfide dyes are frequently used where it is necessary to get a color very resistant to washing. For lists of the individual dyes and details of their application to leather, the reader should consult the various practical handbooks on leather dyeing.

The shade of colored leathers may be darkened, or "saddened," by drumming them in solutions of salts of iron, copper, or other heavy metals. In the production of black leathers, it is common to drum the leather first in a slightly alkaline solution of logwood extract and then in a solution of ferrous sulfate to develop the black. This is often topped by a second dyeing with some artificial black dyestuff.

After the leather has been dyed, it is customary to rinse it in cold water, smooth it out by slicking, lightly oil the surface, and then dry it.

The chemistry of leather dyeing has not yet overtaken the art, although the process is primarily a chemical one. The effect obtained from a given color bath is a function of pH value, concentration, temperature, etc., but the literature contains no record of investigations of leather dyeing under rigidly controlled conditions of pH value, etc., like those on tanning described in Chapters 11 to 14. One may infer that similar principles are involved in both tanning and dyeing.

Finishing.

For descriptions of the numerous mechanical operations and machines used in making leather, including splitting, shaving, slicking, samming, drying, staking, rolling, brushing, boarding, plating, glazing, and embossing, reference should be made to books treating the subject from a more obviously practical viewpoint, like those of Procter,[7] Lamb,[8] and Rogers.[9]

When the leather has been dried, after coloring, it is subjected to various mechanical operations in order to give it the desired physical properties. Ordinary shoe upper leather is coated with a size or finish in order to make it water repellent and more pleasing to the eye. These finishes usually have as a base an aqueous dispersion of gelatin, casein, blood albumin, egg albumin, gum tragacanth, or Irish moss, and are often mixed with colors or pigments. Another popular finishing material consists of a mineral pigment ground in a solution of shellac and borax in water; this is sprayed onto the grain surface of the leather by means of an atomizer.

Patent leathers are coated with a varnish made from boiled linseed oil, driers, and pigments. The leather is dried in a hot oven after the varnish has been applied. The surface is then rubbed smooth and a second coat applied, after which it is again dried in the oven. This may be repeated several times to get the desired effect. The surface of the leather is finally exposed to the sun or to ultra-violet rays for several hours.

Suede or ooze calf leathers are made from the skins of slinks, chrome tanned, colored, and finished on the flesh side. The so-called buck leathers are made from chrome tanned cow hide, split to give a sufficiently thin layer, including the grain. The grain is buffed on an emery wheel and then dusted with a dry pigment. The names of many of the commoner leathers indicate the method of finishing rather than the animal furnishing the skin.

[7] Principles of Leather Manufacture. H. R. Procter. D. Van Nostrand, New York (1922).
[8] Leather Dressing. M. C. Lamb. Leather Trades Publishing Co., London (1909).
[9] Practical Tanning. A. Rogers. Henry Carey Baird & Co., New York (1922).

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